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Exploring the Effects of Different Classroom Environments on the Learning Process.

Synthesis of Thiazole-Linked Porous Organic Polymers for CO_2 Separation and Nitro-Aromatics Sensing.

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Abstract.

When attempting to study the learning process of undergraduate chemistry student, the classroom and any interaction that take place within it constitute the social context of interest. By studying how different approaches can foster different classroom environments, it is possible to approach course design from an informed and scientifically sound perspective. Thus, it becomes necessary to identify and quantify the factors that have a positive or negative effect on the classroom environment. Social comparison concerns, comfort levels and self-efficacy have been shown to be social factors that affect each other as well as the learning process and have therefore been deemed suitable for use in this study. POGIL, a pedagogic approach to teaching chemistry based on small-group work and active learning, has been shown to lead to positive academic outcomes and is currently employed by several faculties at Virginia Commonwealth University. This study seeks to investigate differences in the learning environment observed in lecture and POGIL based chemistry courses, by adapting Micari's survey for measuring social comparison, comfort levels and self-efficacy in small-group science learning.

Reliance on the combustion of fossil-fuels, such as coal, oil and natural gas, as sources of energy has, since the industrial revolution, caused atmospheric CO_2 to increase to the current level of 400ppm by volume; an increase of 25% from the 1960s when monitoring started. Climatologists predict that an increase to 450 ppm would have irreversible effects on the Earth's environment and recommend that, in order to preserve the conditions in which civilization developed, levels be reduced to below 350 ppm. The use of porous organic polymers for capture and separation of CO_2 from industrial sources has been at the forefront of research attempting to curb CO_2 emission into the atmosphere. Benzimidazole based polymers have shown a high selectivity for CO_2.[7] To attempt to improve on the capture abilities of these polymers, we sought to synthesize sulfur containing analogs presenting thiazole moieties. Two such polymers were synthesized using a pyrene-based linker. Furthermore, the pyrene-derived fluorescence of these polymers enabled their use as chemosensors targeting nitroaromatic compounds and mercury ions.

Exploring the effect of different classroom environments.

Background:

As far back as the work of the Greek philosopher Aristotle, humans have been referred to as social animals.[1] However, the social moniker was not extended to learning which is a fundamentally human process, until the introduction of social learning theory by Albert Bandura in the 1960's.[2] Research on the theory of learning had, until then, been dominated by Pavlov's classical conditioning and Skinner's operant conditioning. These frameworks studied the dependency of animal behavior on reinforcements and stimuli, and contended that all human behavior could be attributed to the same principles.[3] Bandura postulated that the human capacity for learning extends beyond the behavioral mechanism of reward and punishment. His framework states that learning is a cognitive process taking place in a social context. Social context is defined as the combination of one's cultural background and preconceived notions, as well as the individuals and the social situations that they interact with.[3]

When attempting to study the learning process of undergraduate chemistry students, the classroom, and any interaction that take place within it, constitute the social context of interest. By studying how different approaches can foster different classroom environments, it is possible to approach course design from an informed and scientifically sound perspective. Thus it becomes necessary to identify and quantify the factors that have a positive or negative effect on the classroom environment. Social-comparison concerns, comfort, and self-efficacy have been shown to be social factors that affect each other as well as the learning process, and have therefore been deemed suitable for use in this study.[4,5]

Social-comparison concerns address how students might feel intimidated by worrying that they are less talented, or perform worse than their classmates. The achievement-focused environment of a chemistry course is conductive to upwards-comparison with peers who are seen as more competent. The simple act of perceiving himself as inferior to his peers is often sufficient to affect a student's performance negatively.[6] Comfort levels indicate how comfortable a student is at being oneself during in-class interactions, and is shaped primarily by the nature of a student's interaction with his peers.[4] Academic Self-Efficacy describes a student's belief that he holds in regard to his own ability to perform well in a given academic environment.[7] Perception of self-efficacy has been shown to affect individuals' choice of activities and settings, as people tend to avoid situations they believe exceed their capacities. Furthermore, high self-efficacy has been shown to lead to improved academic performance by increasing coping efforts for those who engage in activities above their level.[5,7]

Statement of the problem:

POGIL (Process Oriented Guided Inquiry Learning) is a teaching method that relies on a learning cycle of exploration, concept invention, and application. Students are provided with an initial model and then explore the concept in small groups, through carefully-crafted class activities, and look for patterns within that model. The activity leads students to the creation of new concepts by asking pointed questions. The new concepts are then applied to problems that lie beyond the scope of the initial model. The process oriented aspect of POGIL requires students to achieve their own conclusions without being handed the correct answer, promoting process oriented skills such as communication, teamwork, problem solving, critical thinking, and management, which are highly sought by employers. Furthermore the guided inquiry aspect provides scaffolding for lifelong learning beyond the classroom, encourages in-depth understanding of the concepts, and provides students with a sense of ownership of the material.

The instructor assumes the role of facilitator, and addresses students' questions by encouraging critical thinking and discussion amongst the groups.[8]

The POGIL approach seeks to add a constructivist approach to the traditional exposition based lecture, in which teaching is seen as a direct transfer of information from teacher to student.[9] POGIL, on the other hand, employs a theoretical framework rooted in Piaget's constructivist model, according to which the acquisition of knowledge requires the learner to challenge their existing concepts with new ones.[10] The learning process thus becomes personalized to each individual learner. Furthermore, the social aspect of POGIL, which requires students to interact with their peers much more than lecture courses, promotes the acquisition of collaborative skills and cooperative problem-solving.[11] The social aspect of learning employed by POGIL is also intrinsic to Vygotsky's social development theory, according to which social interaction is a fundamental element to cognitive development. It also incorporates Vygotsky's concept of the zone of proximal development: POGIL's activities are designed to scaffold the inquiry process so that the construction of new concepts is within reach of the individual learner.[12]

Several sections of general, organic and physical chemistry at Virginia Commonwealth University (VCU) are taught using POGIL. This, combined with the large population of undergraduate students enrolled in chemistry courses (over 3,000), and the high degree of diversity (49% of students belong to a racial/ethnical minority; 57% of students are female), makes VCU an ideal campus for a quantitative study of the benefits of POGIL.[13]

We seek to study how the different classroom environment of a POGIL-based chemistry course influences students' levels of social-comparison concerns, comfort, and academic self-efficacy compared to traditional lecture-based courses. Furthermore, this project seeks to investigate how the classroom environment affects academic achievements. In the literature, students have been found to report resistance and skepticism when required to work in groups.[11,14,15] There is also the risk that mandatory group work may further aggravate any feelings of difference and exclusion for members of under-represented demographics, and lead them to perceive a degraded classroom environment. It is therefore important to study whether these potential pitfalls may cause POGIL to produce unintended negative outcomes. The following hypotheses were put forth to be investigated:

H1: A positive learning environment can be fostered by using POGIL in chemistry courses.

H2: The benefits of POGIL will be most pronounced for women, minorities, and first generation college students.

H3: A positive learning environment will correlate with an increase in academic performance.

These hypotheses were based on the social and active-learning nature of a POGIL-taught course. By interacting with their peers through the learning process students are expected to develop a stronger sense of community, and in turn experience an enhanced social environment in the classroom. Active-learning approaches have also been known to have a higher beneficial impact for under-represented groups, leading to the expectation of increased academic performance for minorities, women, and first generation college students.[14,16–20]

Experimental Methods

Study Design and Participants:

This study was submitted for review by the VCU institutional review board (IRB# HM20005357) and was approved as following guidelines for ethical research involving human participants. The data-collection instrument was adapted from Micari's survey for the study of intimidation in peer-led small learning groups.[4] Any reference to the small learning groups was changed to the context of a classroom environment. The instrument consisted of 18 items measuring social-comparison concern, comfort being oneself in the classroom, and self-efficacy for the chemistry course the student was currently enrolled in. These items, shown in Table 1 in the order they were administered, were rated by the participants on a 0-100 slider scale. The factor loadings accompanying each survey item are explained in the statistical analysis section. Additionally, the instrument contained four multiple-choice demographic questions, identifying the participants' gender, class level, ethnicity, and status as a first generation college student.

Table 1. Factor Loading for Survey Items, n = 788.

Survey Items	Factors Loading		
	Social-Comparison (SC)	Comfort being oneself (C)	Self-Efficacy (SE)
I feel different from the other people in this class.	0.742		
I often leave the class feeling like I am not as smart as others.	0.644		
I often feel intimidated to participate in the class.	0.525		
I often leave the class feeling like I am the only one who doesn't understand the material well.	0.620		
I worry about getting things wrong in front of the class.	0.317		
I have generally understood the material as well as the others understand it.	-0.348		
I feel comfortable offering my own ideas in this class.		0.736	
I feel like it's okay to make mistakes in front of others in my class.		0.869	
I feel like it's okay to make mistakes in front of others in my class.		0.345	
I feel like it's okay to ask dumb questions in the class.		0.747	
I'm confident I can do an excellent job on the assignments and tests in this course.			0.868
I'm certain I can understand the most difficult material presented in the readings for this course.			0.833
I'm confident I can learn the basic concepts taught in this course.			0.734
I expect to do well in this class.			0.888
I'm certain I can master the skills being taught in this class.			0.877
I'm confident I can understand the most complex material presented by the instructor in this course.			0.858
I believe I will receive an excellent grade in this class.			0.899
Considering the difficulty of this course, the teacher, and my skills, I think I will do well in this class.			0.899

The instrument was administered twice, during the first and last month of the spring 2016 semester. Students enrolled in general, organic, and physical chemistry courses at VCU were invited to participate via email. The survey was also attempted during the fall 2015 semester, however the participation level was too low for statistical analysis. During the spring 2016 semester, participation was encouraged via a raffle for three $100 gift cards to the VCU bookstore. This led to a 40% increase in participation at the beginning of the semester and a 300% increase in participation at the end of the semester compared to the fall 2015 study. Previous research shows that including a raffle as incentive does not affect the responses.[21,22] Additional data such as final letter grades and GPA were obtained from the VCU eServices system.

Study data were collected and managed using REDCap electronic data capture tools hosted at Virginia Commonwealth University. REDCap (Research Electronic Data Capture) is a secure, web-based application designed to support data capture for research studies, providing 1) an intuitive interface for validated data entry; 2) audit trails for tracking data manipulation and export procedures; 3) automated export procedures for seamless data downloads to common statistical packages; and 4) procedures for importing data from external sources.[23] The collected data were manipulated using IBM's SPSS 13.

Statistical Analysis

The internal consistency of the 18 survey items was tested using Cronbach's α. Factor analysis was employed to assess whether the survey items correctly measured the desired constructs of social comparison, comfort, and self-efficacy. Response scores for each factor were grouped according to the factor loading observed in Table 1, and averaged to provide each participant with a single score in each category. The Pearson *r* correlation and t-tests were used to investigate the relationship between demographics, classroom pedagogy, social concerns, self-efficacy, and academic outcomes. All statistical analysis was carried out using SPSS 23 (IBM, Armonk, NY).

The Cronbach's α and factor analysis were carried out using responses from all course levels, and included data from both the beginning and the end of the semester. This was done in order to meet the large sample size required for these tests (n = 788); and to create a workable framework for the comparison of POGIL and lecture courses. The change in responses over the course of the semester, and the correlation to academic outcomes, were studied using data exclusively from organic and physical chemistry sections (n = 78). Four sections taught by lecture and two sections taught exclusively via POGIL were analyzed. Because none of the general chemistry sections were taught using POGIL exclusively, the data from general chemistry sections was not used for comparison purposes.

Results and Discussion:

Validation and Identification of Factors:

The Cronbach's α test returned a value of 0.933 which indicates a strong correlation between the survey items. Application of factor analysis to the non-demographic items of the initial survey revealed the emergence of three main groupings. Table 1 shows the loading values for each, with higher values indicating a stronger correlation within that group. Three factors were determined by a combination of the loading in Table 1, with a minimum loading of 0.3, a minimum of 1 eigenvalue per factor as shown in Figure 1, and by identifying the area where the slope plateaued. The three factors accounted for 70% of the variance in the data as shown in **Error! Reference source not found.**. The presence of a fourth factor was investigated. However, this only accounted for an additional 5% of the data's variance, at the cost of reducing the loading for several items in the 3rd and 4th factor below the 0.3 threshold, as shown in Supporting Table 1. All analysis was conducted under the assumption of only three factors being present.

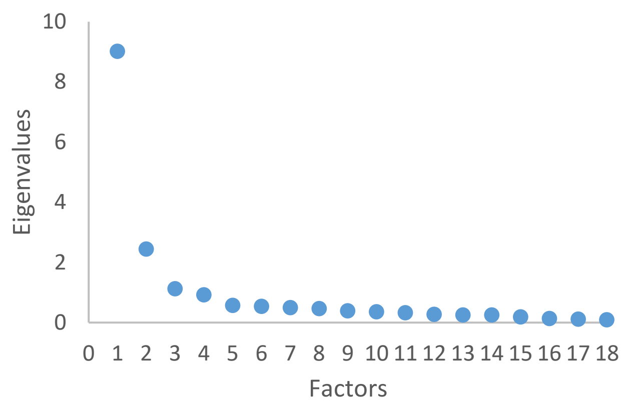


Figure 1. Eigenvalues of factors.

Table 2. Eigenvalues and variance of factors.

	Initial Eigenvalues		
Factor	Total	% of Variance	Cumulative %
1	9.0	50.1	50.1
2	2.4	13.6	63.7
3	1.1	6.2	69.9
4	0.9	5.1	75.0

The major factor identified corresponded to the self-efficacy items, which have been previously validated.[24] The remaining items, which measured intimidation in the classroom, showed the same split into two factors observed by Micari: social comparison and comfort.[4] It is worth noting that the sixth social-comparison item was observed having a negative loading. This was expected because items 1-5 used negative wording, whereas item 6 was a positive statement. The negative loading serves as evidence that participants were answering the survey consistently, rather than choosing random responses.

<u>Pedagogic approach and classroom environment</u>

In order to study the effects of different pedagogic approaches on the classroom environment, the mean of the initial and final responses in Lecture (n = 54) and POGIL (n = 24) sections was calculated. As shown in Figure 2, social comparison concerns were unchanged for lecture, but decreased for POGIL sections. Comfort levels were unchanged for lecture, but increased for POGIL sections. Participants in lecture sections reported a higher initial self-efficacy than those in POGIL sections. However, over the course of the semester self-efficacy decreased in lecture and increased in POGIL sections, leading to higher final self-efficacy in POGIL sections. Because the initial survey was administered during the first two weeks of the semester, it is possible that the difference in initial responses between POGIL and lecture sections may be caused by the difference in pedagogies. Due to the single-semester nature of this study however, it is not possible to determine whether the difference is indicative of any pedagogic effect, or whether it provides different baselines for the different sample groups. Repetition of the study over the course of additional semesters would provide additional evidence as to the nature of the initial difference in responses. Furthermore, the use of follow-up interviews with the study participants would provide an opportunity to determine whether enrollment in a class using a non-traditional pedagogy is responsible for the lower self-efficacy reported initially.[5,25] It is not possible to determine whether initial responses provide significant insight on the different pedagogies, so this study was structured as a longitudinal study to compare the change in responses between beginning and end of the semester.

The mean change in responses, over the course of the semester, was calculated for each participant. A t-test was used to compare the mean of the differences between lecture and POGIL sections. The values for the differences are provided in Table 3. The reduction in self-comparison concerns observed in POGIL sections was found to be statistically significant when compared to the change in lecture sections ($p = 0.032$). No statistical significance was observed when comparing the changes in comfort levels ($p = 0.229$). The increase in self-efficacy reported by POGIL sections was found to be statistically significant different from the decrease reported by lecture sections ($p = 0.001$).

Table 3. Mean change in survey responses over the course of the semester.

	Means of the change		
	Social Comparison*	Comfort Level	Self-Efficacy*
Lecture (n=54)	0.06 ± 1.87	1.14 ± 2.14	-7.80 ± 2.65
POGIL (n=24)	-6.98 ± 3.69	4.39 ± 4.43	9.78 ± 5.70

*significant to α = 0.05

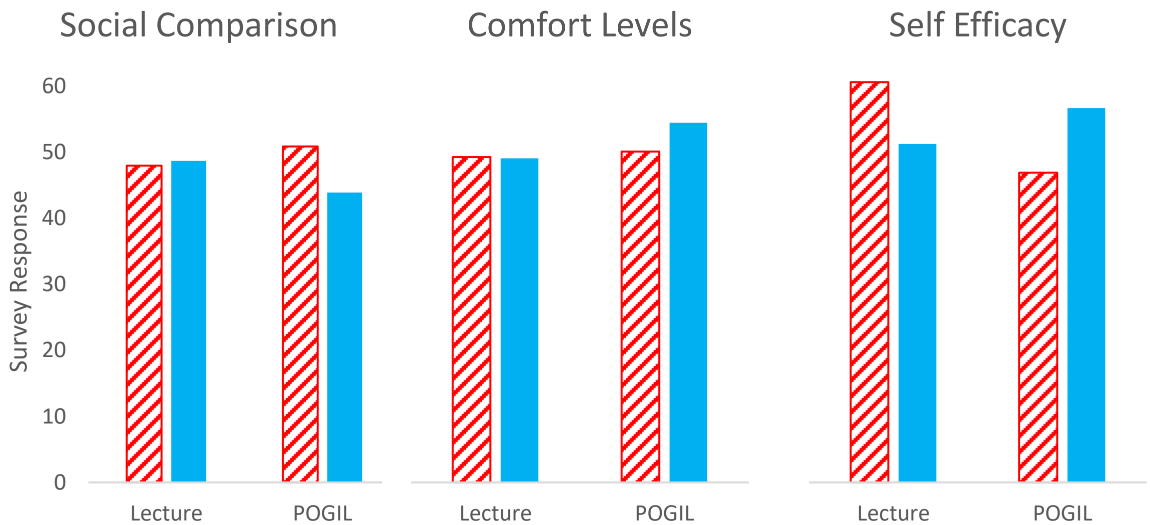


Figure 2. Comparison of survey responses for the beginning (red dashes) and end (solid blue) of the semester.

The normalized count of respondents that reported an increase or decrease in their survey items was used as an additional tool to visualize these results. Figure 3 shows that approximately two third of respondents reported positive changes in POGIL sections across all survey items. Respondents in lecture sections reported an even split in both social-comparison concerns and comfort levels, two third of respondents reported a decrease in self-efficacy. The changes for individual sections were also evaluated and, no statistical significance was observed due to reduced sample size. The same trends were observed in each of the four lecture sections and both POGIL sections. This suggests that these effects were not due to differences in instructor, or their implementation of the chosen pedagogy.

These results support hypothesis 1: the mean change of social-comparison concerns and self-efficacy both indicate a positive learning environment being fostered by using POGIL in chemistry courses, and are in agreement with previous studies.[14,16–20] Furthermore they indicate that working in small groups did not worsen social comparison concerns. The normalized count also shows that up to two thirds of respondents enrolled in a POGIL chemistry course report a positive change in each of the survey items used to study classroom environment.

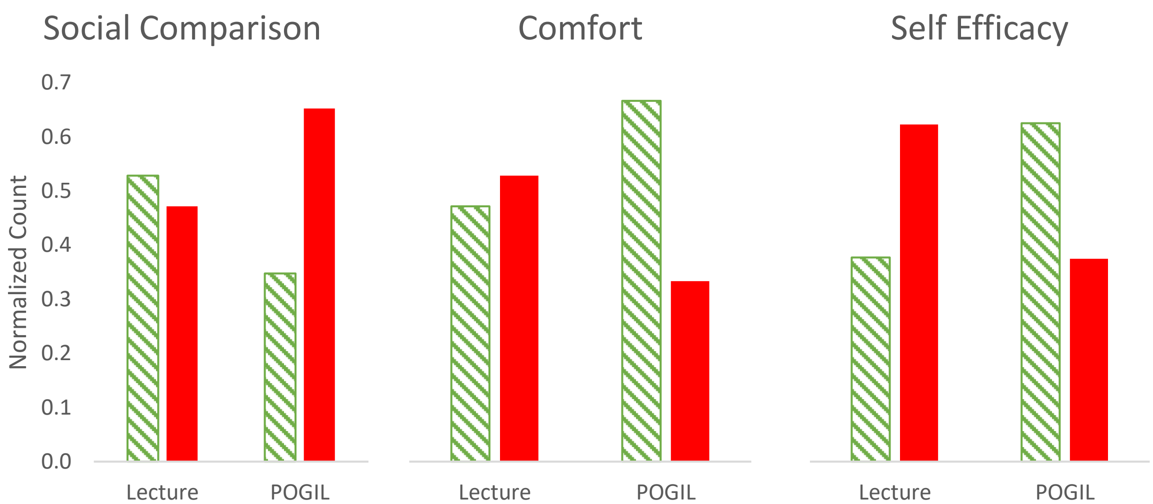


Figure 3. Normalized count of respondents reporting an increase (dashed green) or decrease (solid red) in survey responses.

<u>Demographic Makeup</u>

Gender, ethnicity, and family education were identified as demographic factors which could impact the classroom environment perceived by the participants. In order to study how these factors would affect the responses to the survey items, it was necessary to observe the demographic makeup of the respondent sections. Figures 4-6 provide a graphical representation of demographic distribution. The participants in the POGIL sections (46% male; 54% female) were found to be similar in gender makeup to the overall VCU student population (41% male; 57% female).[26] The lecture sections however, showed a markedly higher response ratio for female participants (26% male; 74% female). The ethnicity of VCU students was evenly split (51% white or Caucasian; 45% minority; 4% not reported)[26] the respondents in POGIL sections were mostly white or Caucasian (71% white or Caucasian; 29% minority) and respondents in lecture section were mostly belonging to a minority (31% white or Caucasian; 69% minority). Family education history was not reported for VCU, but similar makeup was observed for lecture (28% first generation college student) and POGIL (38% first generation college student) sections. Table 4 provides the sample size for each demographic factor. It is to be noted that due to the limited sample sizes involved, any statistically significant difference observed, only indicated weak statistical power.

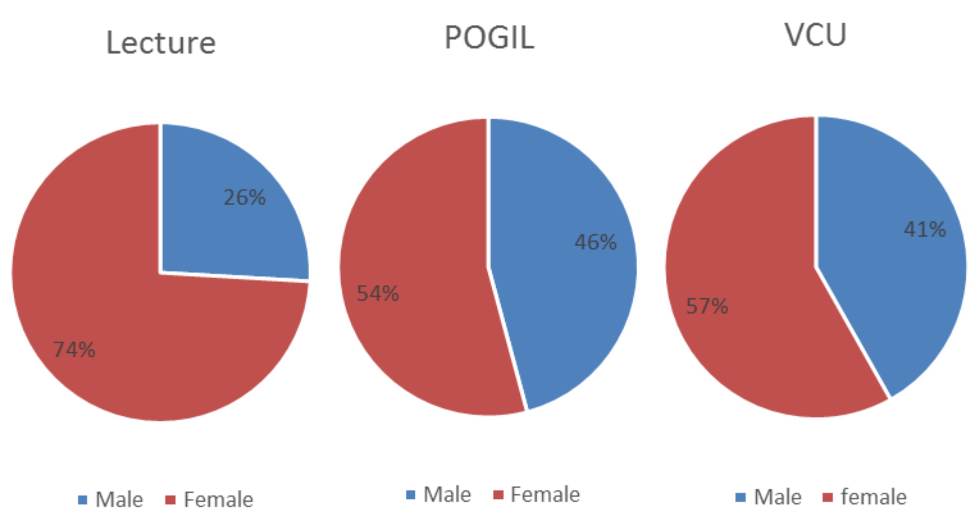


Figure 4. Gender Makeup of Respondents and VCU Students.

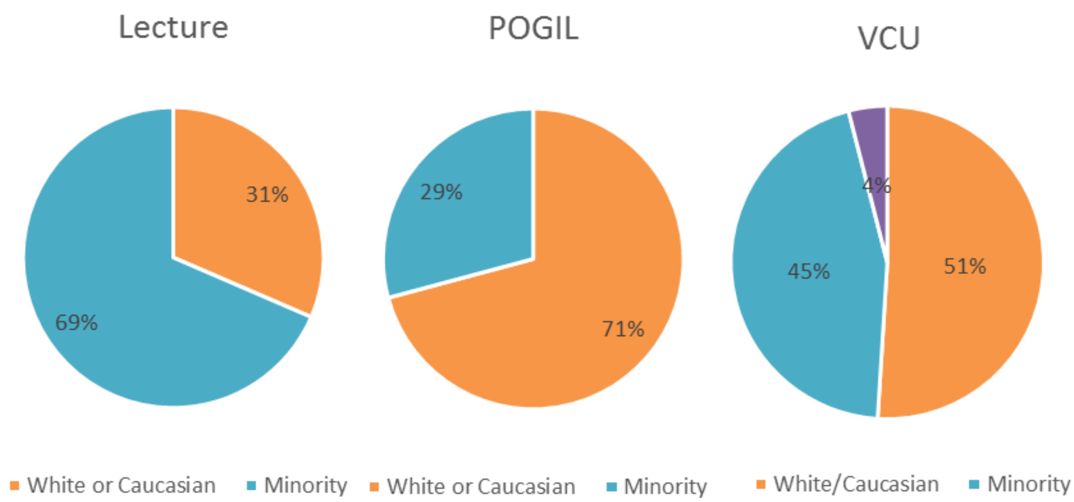


Figure 5. Ethnic Makeup of Respondents and VCU students.

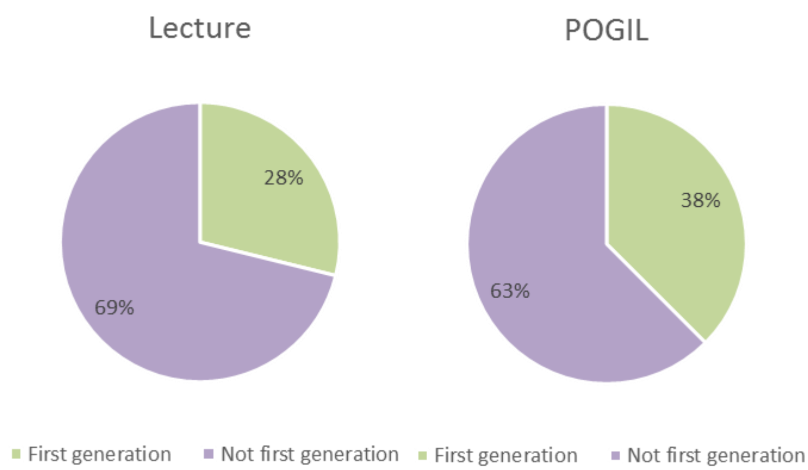


Figure 6. Family Education History of Participants.

Table 4. Sample size for comparison of changes over the semester.

	Sample Size, n					
	Gender		Ethnicity		Family's Education	
	Male	Female	White	Minority	Bachelor'	First generation
Lecture	14	40	17	37	37	15
POGIL	11	13	17	7	15	9

Effect of Demographics on Perceived Classroom Environment.

Pearson's correlation and t-tests showed that no statistically significant difference was observed in the change of survey responses between different demographics when disregarding the pedagogic approach used. Comparing responses of lecture and POGIL sections may provide insight on the benefits of active learning for historically under-represented demographics.

Figure 7 shows initial and final responses grouped by gender and pedagogic approach; the mean changes are summarized in Table 5. No statistical difference was observed for male respondents when comparing across POGIL (n = 11) and lecture sections (n = 14). It is however important to note that that male respondents in lecture sections reported a significantly smaller decrease in self-efficacy than the overall lecture sections as seen in Table 3. A statistically significant difference was observed for female respondents when comparing social-comparison concerns (p = 0.016) and self-efficacy (p = 0.006) between POGIL (n = 13) and lecture sections (n = 40). Female participants reported no change in social-comparison concerns in lecture sections, those in POGIL sections reported a ten point reduction. Female participants reported a marked decrease in self-efficacy in lecture sections, and a marked increase in POGIL sections, mirroring the overall trend observed in Table 3.

These results support hypothesis 2, showing that female respondents reported improvements to their social-comparison concerns and self-efficacy when enrolled in POGIL chemistry courses. This is in agreement with previous studies on the use of active-learning pedagogies.[14,16–20] No statistical difference was observed for male respondents, there was also no indication that men were negatively affected by enrollment in POGIL chemistry courses.

Table 5. Effect of gender upon survey item changes.

	Means of the change over the semester.					
	Male			Female		
	Social Comparison	Comfort Level	Self-Efficacy	Social Comparison*	Comfort Level	Self-Efficacy*
Lecture	0.19 ± 4.85	5.66 ± 5.70	-1.08 ± 5.43	0.01 ± 1.93	-0.44 ± 2.08	-10.15 ± 2.99
POGIL	-2.57 ± 4.75	3.47 ± 6.33	10.33 ± 5.44	-10.71 ± 5.46	5.15 ± 6.42	9.32 ± 9.69

*significant to $\alpha = 0.05$

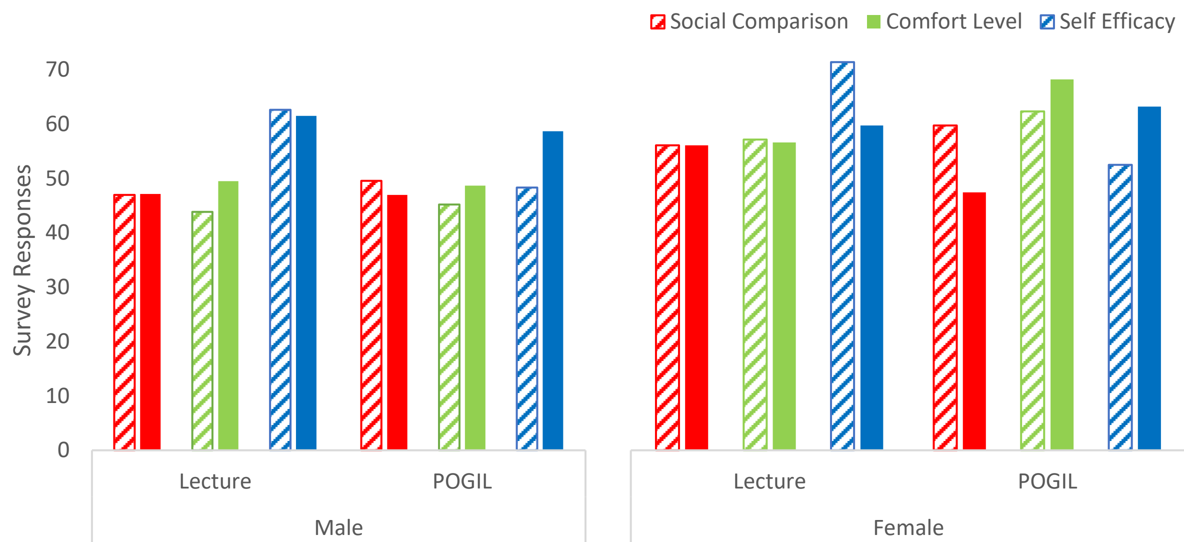


Figure 7. Survey responses by gender and pedagogy. Initial responses are shown as dashed columns, final responses as solid columns.

Figure 8 shows initial and final responses grouped by ethnicity and pedagogic approach; the mean changes are summarized in

Table **6**. It is important to note that, although the survey differentiated between minority ethnicities, for the purpose of analysis all minority respondents were grouped together. This was necessary due to the low sample size, which would be further fragmented if analyzing each individual ethnicity separately. This approach was justified by the fact that each minority shares the trait of being an under-represented group. No statistical difference was observed for minority respondents when comparing across POGIL (n = 7) and lecture sections (n = 37). Self-efficacy for minority respondents in POGIL sections was not observed to have the same marked increase as the overall POGIL sections seen in Table 3. White or Caucasian respondents reported statistically significant d for all three factors between POGIL (n = 17) and lecture (n = 17) sections. Social-comparison concerns were increased in lecture but lowered in POGIL section (p = 0.01). Comfort levels (p = 0.049) and self-efficacy (p = 0.013) both decreased in lecture and increased in POGIL sections. This does not support hypothesis 2. Although these results indicate that white or Caucasian respondents perceived the main benefits from the use of active-learning pedagogies, it should be noted that no detrimental effect was observed for minority participants. In order to ensure that the particularly small sample size for minorities enrolled in POGIL sections was not to blame for the lack of significance, the sample size was artificially doubled (n = 14) and the t-tests were repeated. However, no change in significance was observed.

Table 6. Effect of ethnicity on survey item changes.

	Means of the change over the semester.					
	White or Caucasian			Minority		
	Social Comparison*	Comfort Level*	Self-Efficacy*	Social Comparison	Comfort Level	Self-Efficacy
Lecture	5.23 ± 2.84	-6.19 ± 3.56	-6.50 ± 3.67	-2.32 ± 2.33	4.51 ± 2.49	-8.39 ± 3.51
POGIL	-8.18 ± 4.67	4.82 ± 5.38	13.19 ± 7.56	-4.07 ± 6.02	3.32 ± 8.41	1.50 ± 6.35

*significant to α = 0.05

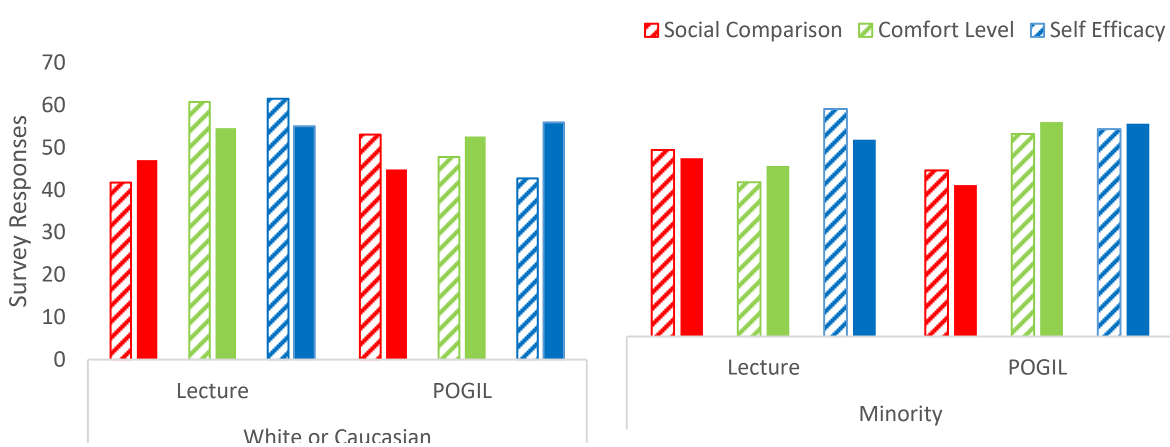


Figure 8. Survey responses by ethnicity and pedagogy. Initial responses are shown as dashed columns, final responses as solid columns.

Figure 9 shows initial and final responses grouped by family education and pedagogic approach; the mean changes are summarized in Table 7. First generation college students reported no statistically significant difference in any of the factors between POGIL (n = 9) and lecture (n = 15) sections. Unlike the other demographic categories, no trend comparable to the overall pedagogy study in Table 3 were observed, with all factors reporting negligible change. Participants with at least one college-educated parent or guardian reported statistically significant changes in social-comparison concerns (p = 0.008) and self-efficacy (p = 0.0005). Participants from college-educated families showed the same trends as the overall study in Table 3, with social-comparison concerns decreasing more in POGIL (n = 15) than in lecture (n = 37) sections, and self-efficacy decreasing in lecture but increasing in POGIL sections. These results did not support hypothesis 2, as first-generation college students reported similar changes regardless of pedagogy used. However, participants whose immediate family members had completed at least a Bachelor's degree saw the most pronounced positive effects of all demographic groups when taught via active-learning strategies. Although the implementation of active-learning pedagogies has been reported to encounter resistance and skepticism from students, access to a support structure that is familiar with the challenges of college education might provide students with the tools necessary to succeed when exposed to novel learning strategies.[11,14,15] In order to gain further confidence as to the reason for this discrepancy, future research should include interviews with the participants.

Table 7. Effect of family education on survey item changes.

	Means of the change over the semester.					
	At least one parent with Bachelor's			First generation college student		
	Social Comparison*	Comfort Level	Self-Efficacy*	Social Comparison	Comfort Level	Self-Efficacy
Lecture	1.49 ± 2.38	1.47 ± 2.29	-9.73 ± 3.49	-1.42 ± 3.02	-1.45 ± 5.02	-3.89 ± 3.97
POGIL	-10.57 ± 4.96	9.70 ± 5.65	16.37 ± 7.80	-1.00 ± 5.05	-4.47 ± 6.49	-1.19 ± 6.88

*significant to α = 0.05

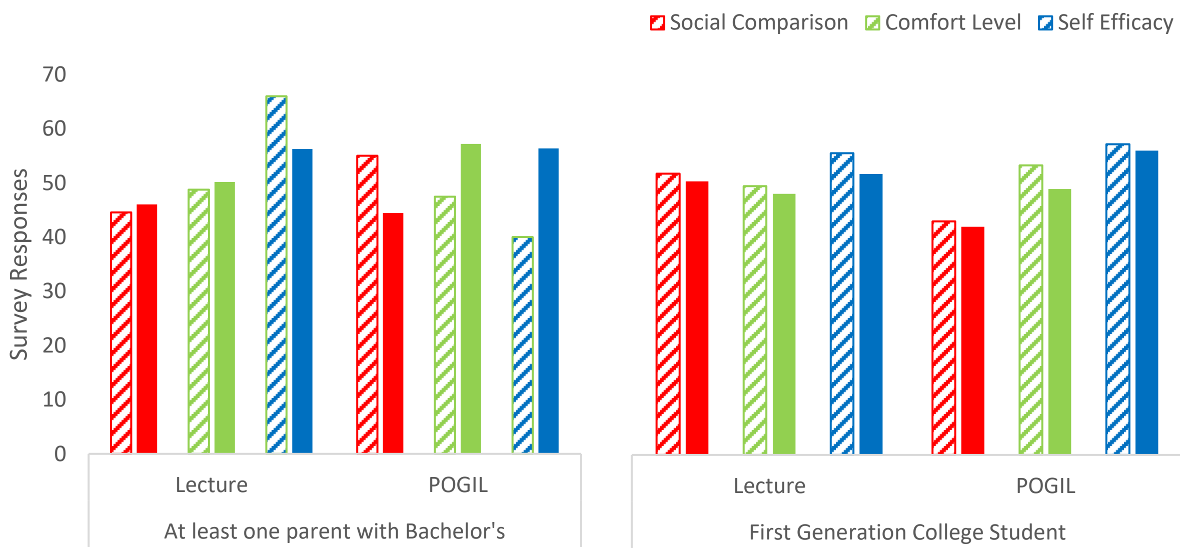
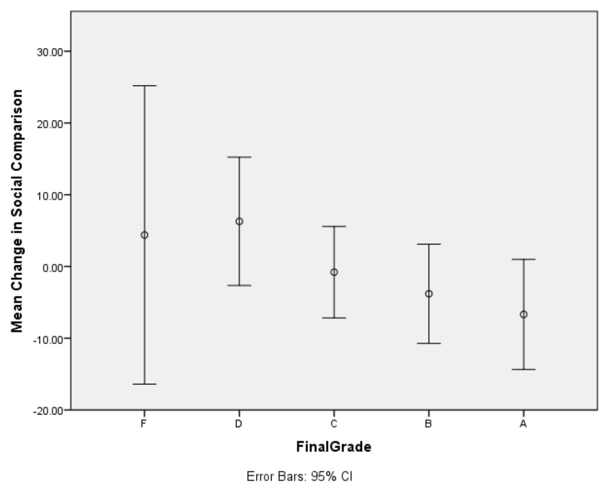


Figure 9. Survey responses by family education and pedagogy. Initial responses are shown as dashed columns, final responses as solid columns.

Classroom Environment and Academic Outcomes.

Pearson's *r* correlation was used to study the relationship between classroom environment (as measured by the change in responses) and academic outcomes (measured by GPA and final letter grade). The GPA of each student was obtained after the completion of the spring 2016 semester. No correlation was found between GPA and survey responses ($n = 58$), which was likely due to the inability to normalize GPA to account for different enrollment and academic paths of the participants. Final letter grades were obtained from the chemistry course the respondents were enrolled in for the spring of 2016. Table 8 shows that the change in social-comparison concerns ($p = 0.31$; $r = -0.254$), comfort level ($p = 0.002$; $r = 0.392$), and self-efficacy (p = 0.039; r = 0.240) were all correlated with final letter grades with a medium effect size (n = 58). Figure 10 shows that the change in social-comparison was negatively correlated with final letter grade. Changes in comfort-level and self-efficacy were positively correlated with final letter grade. These results support hypothesis 3, suggesting that a positive learning environment, identified as a decrease in concerns and an increase in comfort and self-efficacy, correlates with increased academic performance.[14,16–20]



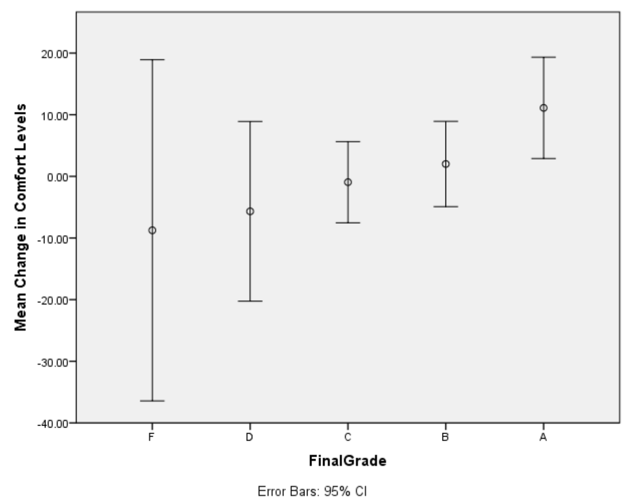


Table 8. Pearson's r correlation of academic performance and factors.

	Pearson's r		
	Social Comparison	Comfort Level	Self-Efficacy
Letter Grade	-0.254*	0.392**	0.240*
GPA	0.008	0.121	0.108

*significant to α = 0.05
**significant to α = 0.001

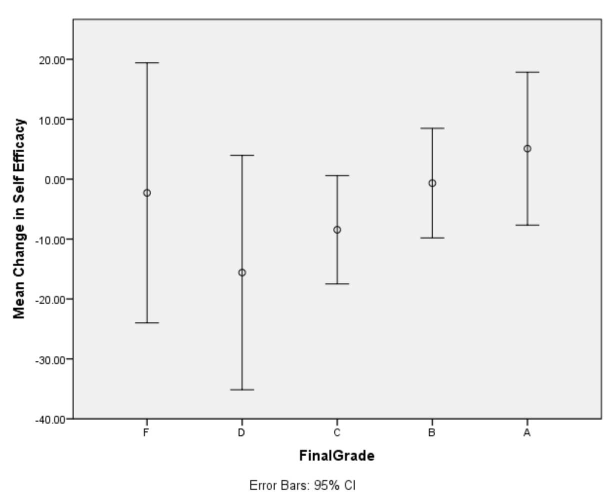


Figure 10. Correlation of final letter grade and social-comparison concerns (top left), comfort levels (top right) and self-efficacy (bottom right).

Conclusions:

A survey asking participants to rate 18 items, relating to classroom environment and self-efficacy, was administered to all undergraduate chemistry students at Virginia Commonwealth University during the 2016 spring semester. The study was approved by the VCU institutional review board (IRB# HM20005357) and the survey was administered online using REDCap. Responses from students enrolled in four organic and physical chemistry sections taught via lecture and two sections taught exclusively via POGIL were analyzed to compare the two different pedagogies.

It was hypothesized that the use of POGIL in chemistry courses would foster a positive learning environment. This hypothesis was confirmed by an observed decrease in social-comparison concerns and an increase self-efficacy for participants enrolled in the POGIL sections. This is consistent with previous studies which suggest that small-group, active-learning pedagogies are useful in creating a sense of community, encouraging the development of process skills, and empowering students to take personal ownership in learning.[14,16–20]

It was also hypothesized that benefits observed in POGIL would be most pronounced for women, under-represented minorities, and first generation college students. Comparing the responses for male and female participants, it was found that women in POGIL sections reported decreased social-comparison concerns and increased self-efficacy, whereas men did not report statistically significant differences. These results supported the hypothesis and are in agreement with other studies on social, active-learning. [14,16–20] Alternately, when comparing ethnicities, white or Caucasian respondents reported improvements in all three factors when enrolled in POGIL courses, however no statistically significant benefit over lecture was observed for minority students. Furthermore, first generation college students did not report any differences between lecture and POGIL, whereas those with at least one college educated parent reported decreasing social-comparison concerns and the most marked increase in self-efficacy than any other demographic, when enrolled in courses taught via POGIL. It is interesting to note that students from college-educated families in POGIL sections reported significantly lower initial self-efficacy than any other group, but the increase over the course of the semester brought their final self-efficacy to similar levels as the other groups. This seems to suggest that resistance and skepticism towards novel learning strategies is initially more pronounced amongst those whose support structure has been educated using traditional methods. Having support from college-educated parents, however, seems to provide these students with the tools necessary to adapt to the new challenges presented.[11,14,15]

Finally, it was hypothesized that a positive learning environment would correlate with increased academic performance. This was supported by finding moderate correlations between final letter grade and each survey factor. Higher letter grades were found to be correlated with lowering social-comparison concerns, increasing comfort levels and increasing self-efficacy, all indicative of a positive learning environment, suggesting that the achievement of a positive learning environment, as identified in this study, is an endeavor worth pursuing.[14,16–20]

POGIL was found to be an effective pedagogy, in undergraduate chemistry classrooms, to foster a positive learning environment and contribute to students' academic success. Even in those cases where the use of POGIL did not lead to significant improvements in social-comparison concerns, comfort levels, or self-efficacy, it is worth noting that requiring students to work in small groups did not cause a worsening of social comparison concerns. This study adds to the expanding literature on small-group, active-learning pedagogies, and provides evidence of POGILS's usefulness to prospective adopters.

Future studies should attempt to investigate the cause of the discrepancy in initial responses between POGIL and lecture sections. This may be accomplished by repeating the survey in new semesters to see whether the same discrepancy occurs across semesters, and by conducting interviews with participants to supplement the data collection with students' accounts of how they perceived the use of an active-learning small-group pedagogy.[25] Furthermore, while this study concentrated on the demographic composition of the sections as a whole, future studies should collect data on the demographic composition of each small group. It would be of interest to determine how students are affected by being part of demographically diverse or homogeneous groups. Understanding of the effect of small groups' makeup would provide important insight for POGIL instructors, in whether to assign group membership or to allow students to pick their own groups.

Synthesis and characterization of thiazole-linked polymers.

Background:

Reliance on the combustion of fossil fuels (such as coal, oil and natural gas) as sources of energy has, since the industrial revolution, caused atmospheric CO_2 to increase to the current level of 400ppm by volume. This is a 25% increase from the 1960s, when monitoring started.[27] Climatologists predict that an increase to 450 ppm would have irreversible effects on the Earth's environment and recommend that, in order to preserve the conditions in which civilization developed, levels be reduced to below 350 ppm.[28]

As clean solutions for energy production have become more financially viable, they have begun to challenge traditional fossil fuels-based methods.[29] However, in order to avoid reaching the 450 ppm threshold, there is still great need to develop technologies capable of reducing the CO_2 emissions of current energy sources, as 87% of global energy needs are being met by combustion of fossil-fuels.[30] The difficulty in the capture and sequestration of CO_2 lies in the need to separate it from other gases. Flue gas, the exhaust of fossil fuel power plants, is composed of 10-15% CO_2 and 70% nitrogen, and accounts globally for 33-40% of anthropogenic CO_2 production.[31]

Efforts to diminish greenhouse gases from energy sources have concentrated on switching to cleaner fuels such as methane, which yields significantly lower amounts of CO_2 to produce the same energy as an equivalent coal or oil-based process. Current sources of methane, however, consist of extracting natural gas (with a composition of approximately 80-95% methane and 5-10% CO_2) or recovering landfill gas from municipal and industrial sources (with a composition of 40-60% methane and 40-60% CO_2).[32]

In order to meet the goals set by climatologists, it has become apparent that lowering the emissions by using cleaner fuels and renewable energy is no longer sufficient.[27] As a result, techniques to capture the CO_2 released by current energy sources have received a great deal of attention. Current industrial applications favor an absorption technique known as amine scrubbing, in which aqueous solutions of various alkyl-amines are used to absorb CO_2 in the solution in the form of carbamate salts.[33] While the reaction is reversible, allowing for the regeneration of the amine solution, the amines are both toxic and corrosive. Furthermore, reversing the bonding between the capture medium and the CO_2 molecules requires considerable amounts of energy, which decreases the overall efficiency of the process. To circumvent this issue, researchers have turned to the study of adsorbent materials that capture CO_2 molecules via weak physical interactions. Due to the reliance of physisorption on van der Waals interactions, instead of chemical bonding, the heat of adsorption is strongly diminished. Since regeneration of the adsorbent requires overcoming the heat of adsorption, physisorption techniques have an efficiency and economical advantage over chemical capturing methods.[34]

In order to develop new adsorption media, certain properties must be kept in consideration: high CO_2 uptake is necessary to ensure large-scale capture is possible; high selectivity for CO_2 promotes efficiency; strong chemical and thermal stability is required to withstand industrial applications; desorption kinetics must be favorable to make regeneration economically viable. In recent years, the development of physisorption-capable materials that meet these requirements has turned to the design of porous polymers. Various typologies have emerged, with metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and porous organic polymers (POPs) receiving a great deal of attention.[34,35] Of the three categories, POPs emerge as the best fit to the properties identified. POPs are amorphous polymers formed by covalently bonded organic monomers to form hyper-cross-linked structures. Their metal-free nature provides two main advantages over MOFs and ZIFs: the lack of coordinate bonds leads to higher chemical and thermal stability, while the use of lighter elements yields lower-density polymers. Furthermore the modular nature of polymer design allows tuning of the structure for high surface area and advantageous pore size. Functionalization of the pore wall can also be achieved by selecting the appropriate monomers, allowing a great deal of flexibility in targeted design of POPs to fit specific applications These include selective gas separation and storage for hydrogen, carbon dioxide, and methane by developing pore walls that selectively attract only the targeted molecules. Development of heterogeneous and reusable nano-scale reactors for synthetic catalysis by incorporation of existing catalysts within the polymers' superstructures. Design of chemo-sensors with broad interfaces, by using building blocks with photo-physical properties and ones with favorable interactions with the target analytes to produce a polymer with large surface area that combines both properties.[35],[36,37]

Statement of the problem:

Non-functionalized POPs are favorable candidates for use in gas storage due to their high surface area. However, when it comes to selective gas separation, while chemisorption techniques enjoy high specificity, the van der Waals interactions observed in non-functionalized POPs lead to non-selective capture of the gas mixture. In order to selectively capture CO_2 it is necessary to design POPs with functionalized groups tailored for this task. A successful example is the class of POPs known as benzimidazole-linked polymers (BILPs), in which the pore wall is functionalized by the imidazole moiety. By exploiting the interaction between the imidazole's dipole and CO_2's quadrupole, certain BILP designs showcase some of the highest selectivity for CO_2/N_2 reported. A recent theoretical study using density functional theory sheds light on the geometry of this interaction.[38] As seen in Figure 11a, the quadrupole-dipole interaction between CO_2 and the imidazole's imine site is the most favored. According to Figure 11b when two additional CO_2 molecules are introduced, they interact with the carbons on the central ring rather than the protonated nitrogen site of the imidazole.

The goal of this research project is to improve on the imidazole-based strategy for selective CO_2 capture. In order to do so, functionalization of the protonated nitrogen site of imidazole, to achieve an additional site of interaction, appears as a promising approach. This was achieved by substituting the imidazole moiety with thiazole. Due to sulfur's ability to form two bonds, as opposed to nitrogen's three, thiazole-linked polymers will exhibit twice as many functionalized sites as BILPs. Polymers attempting to exploit this additional interaction site have been reported by the El-Kaderi group, which produced benzothiazole and benzoxazole-linked polymers which provided similar CO_2 uptake and heat of adsorption to their previously reported benzimidazole-linked polymer equivalents.[39]

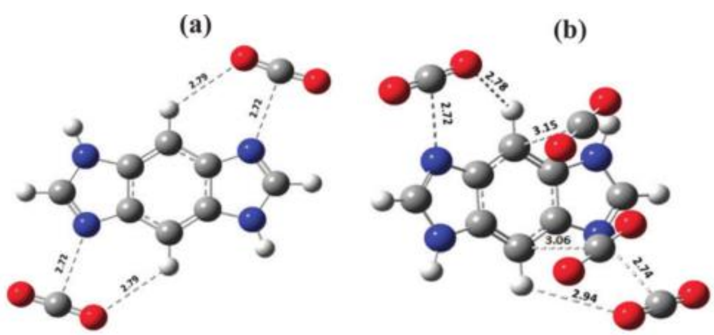
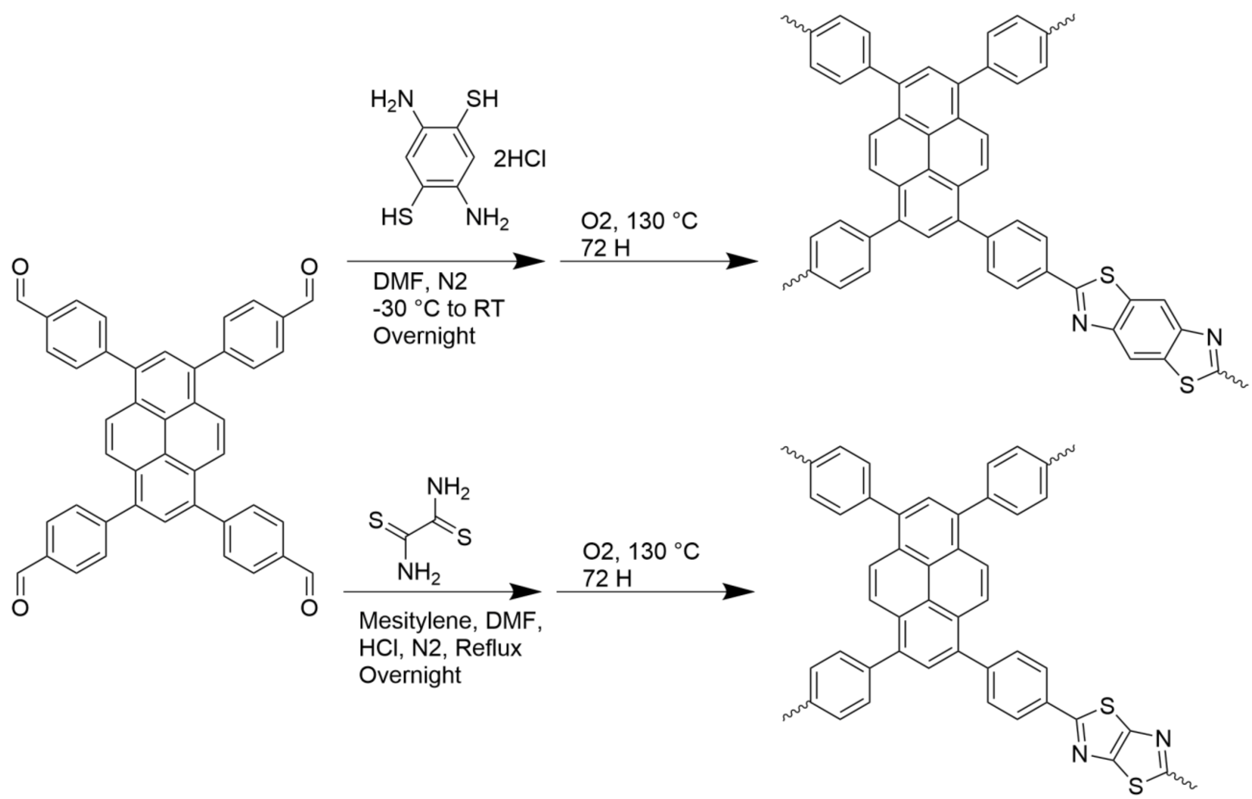


Figure 11. Optimized geometry for the interaction of two (a) and four (b) CO_2 molecules with benzo-biz(imidazole).[38]

In order to maximize potential gains, the thiazole polymers were designed on the template of BILP-10: a polymer with relatively large surface area (780 m^2s^{-1}) and one of the highest reported CO_2/N_2 selectivity (107 at 273 K).[40] The number 10 denotes the presence of a pyrene core. Two polymers were designed: BTLP-10 (benzothiazole-linked) and TzTz-10 (thiazolothiazole-linked). BTLP-10 is BILP-10's sulfur-containing analogue, and its synthesis and characterization should give direct insight into the effects of the additional site of interaction. TzTz-10 is formed by two consecutive thiazoles and its synthesis requires the use of a cheaper, non-air sensitive linker, which could be a decisive advantage in translating its application to industrial scale. Their structures are shown in Scheme 1.



Scheme 1. Synthesis of BTLP-10 (top) and TzTz-10 (bottom) polymers.

Furthermore, pyrene is known to exhibit photoluminescence properties, which are retained when incorporating it in a polymer's structure. Paired with the high surface area of POPs there exists the potential to produce powerful chemosensing tools.[41] The thiazole units, which provide the interaction with CO_2 during gas separation, are also capable of forming hydrogen bonds, which enables a diverse range of potential analytes. A potential application rests in the sensing of 2,4,6-trinitrophenol (TNP) explosive. TNP is ideal for study with BTLP-10 and TzTz-10 because it is capable of interacting with the polymer using hydrogen bonds. The nitro substituents, which are responsible for TNP's reactivity, should also cause quenching of the polymers' fluorescence by delocalizing the framework's π electrons.[37,42] Quenching was studied for TNP as well as the non-explosive species 2-nitrotoluene (NT), 2,4-dinitrotoluene (DNT), 2-nitrophenol (NP) and 2,4-dinitrophenol (DNP). The lower number of nitro substituents in DNP and NP should lead to decreased quenching, while NT and DNT are expected to cause little quenching due to their inability to form hydrogen bonds with the thiazole unit. The incorporation of sulfur atoms on the wall of the polymers' pores also opens up the potential for their use in the sensing and capture of mercury ions to aid in environmental cleanup efforts. Mercury ions are specifically targeted due to sulfur's π-donor's character, which allows for specific soft-soft interaction with mercury's d-orbitals.[43,44] Theoretically this movement of electrons from the polymers' framework toward the mercury ions should lead to the same fluorescence quenching as expected with nitrophenol explosives.

Experimental Methods:

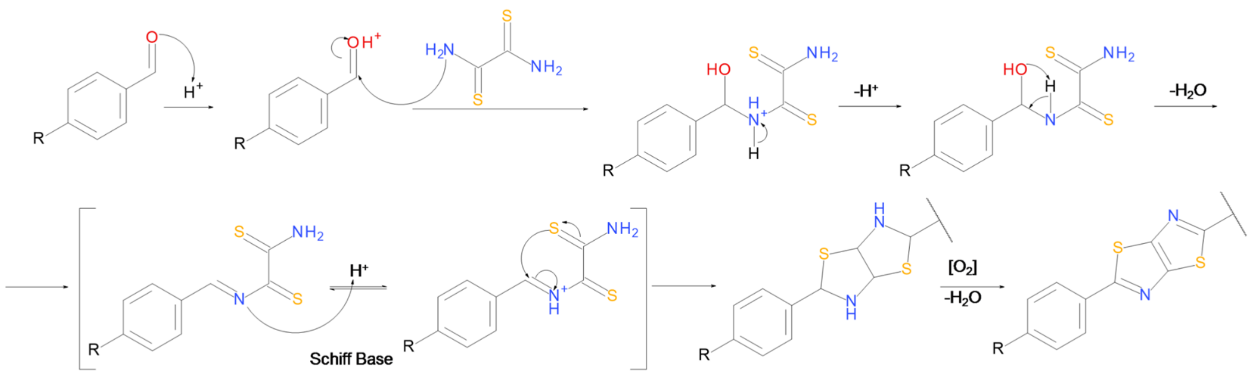
<u>Synthesis of Pyrene Monomer:</u>

Pyrene (5.00 g, 0.0247 mol) was dissolved in nitrobenzene (100 ml) and heated to 120 °C in a reflux apparatus under vigorous stirring. Bromine (5 ml, 0.11 mol) was added dropwise. The solution was kept at 120 °C overnight and cooled to room temperature to yield a light-green precipitate. This was vacuum filtered and washed with ethanol (3 aliquots of 50 ml), and then dried under vacuum to yield 1,3,6,8-tetrabromopyrene (9.97 g, 0.0193 mol, 78%) as a light green powder.[45]

A Schlenk flask (100 ml) was kept under inert atmosphere (N_2) and loaded with tetrakis(triphenylphospene)palladium(0) (0.12 g, 1.0×10^{-4} mol). 1,3,6,8-tetrabromopyrene (1.00 g, 1.93×10^{-3} mol) and 4-formyphenylboronic acid (1.74 g, 1.16×10^{-2} mol) were added. Potassium carbonate (2.1 g, 15 mmol) in dried dioxane (30 ml) was added, and the resulting solution was stirred under N_2 at 85 °C for 72 hours. Hydrochloric acid (80 ml, concentrated) was added to an ice bath (240 ml). The cooled mixture was stirred into the ice bath for several minutes and then vacuum filtered over a medium frit to yield a yellow precipitate. This was washed with hydrochloric acid (2 M, 3 aliquots of 20 ml). Hot chloroform (~500 ml) was used to dissolve the product and pull it through the filter, leaving a sticky white residue behind. The filtrate was washed with aqueous sodium hydroxide (1 M, 3 aliquots of 50 ml), dried over magnesium sulfate, and passed through a chromatography column packed with silica. Excess chloroform was removed with a rotary evaporator. The product was recrystallized from hot chloroform to yield 1,3,6,8-tetrakis(p-formyphenyl)pyrene (TFPP, 0.801 g, 1.29×10^{-3} mol, 67 %) as a yellow crystalline solid.[40] Successful synthesis was confirmed by ^{1}H proton NMR with peaks at 10.16 ppm (4 H; s), 8.18 ppm (4 H; s), 8.09 ppm (8 H; d), 8.04 ppm (2 H; s), and 7.86 ppm (8 H; d). The NMR spectrum is shown in Supporting Figure 1.

Synthesis of Thiazole-Linked Polymers:

The proposed mechanism for the formation of thiazole linked polymers is shown in Scheme 2 The protonated benzaldehyde is subjected to backside attack from the 1,2-aminothiol component of the linker. Rearrangement and subsequent acid-catalyzed dehydration leads to the formation of a Schiff base in the form of a secondary ketimine which, under acidic conditions, experiences ring closure. Introduction of oxygen leads to formation of the thiazole moiety.[46]



Scheme 2. Proposed mechanism for the formation of thiazole linkers.

The synthesis of both pyrene-thiazole polymers is shown in Scheme 1. The synthesis of BTLP-10 was achieved by adapting the condensation reaction previously used for the synthesis of its benzimidazole-linked analog.[40] A Schlenk flask was kept under inert atmosphere (N_2) and loaded with 2,5-diamino-1,4-benzenedithiol dihydroxhloride (0.160 g, 6.5×10^{-4} mol) and dimethylformamide (60 ml). The solution was cooled to -30 °C in an acetone-dry ice bath. A solution of 1,3,6,8-tetrakis(p-formyphenyl)pyrene (205 mg, 3.3×10^{-4} mol) in anhydrous dimethylformamide (30 mol) was added dropwise. The reaction was kept at -30 °C for 4 hours and then allowed to warm up to room temperature overnight. Oxygen was introduced by bubbling air through the solution for 15 minutes. The flask was sealed and placed in an oven at 130 °C for 72 hours. The resulting solid was vacuum filtered over a fine frit and washed with dimethylformamide, hydrochloric acid (2 M), sodium hydroxide (2 M) and water. The polymer was soaked in chloroform for 24 hours, vacuum filtered and dried at 120 °C under vacuum (150 mTorr) to yield BTLP-10 (0.152 g, 41%) as a fluffy light-brown solid.

To synthesize TzTz-10, a Schlenk flask was kept under inert atmosphere (N_2) and loaded with rubeanic acid (3.9×10^{-2} g, 3.23×10^{-4} mol), 1,3,6,8-tetrakis(p-formyphenyl)pyrene (0.100 g, 1.62×10^{-4} mol) and anhydrous dimethylformamide (40 ml). Dry mesitylene (20 ml) and hydrochloric acid (concentrated, 54 µl, 6.48×10^{-4} mol) were added and the solution was stirred under reflux conditions (153 °C). The resulting mixture was cooled to room temperature and had air bubbled through for 15 minutes. The flask was sealed and placed in an oven at 130 °C overnight. The resulting solid was vacuum filtered over a fine frit and washed with dimethylformamide, hydrochloric acid (2 M), sodium hydroxide (2 M) and water. The polymer was soaked in chloroform for 24 hours, vacuum filtered and dried at 120 °C under vacuum (150 mTorr) to yield DTLP-10 (0.072 g, 52%) as a fluffy orange solid.

Results and Discussion:

Characterization of Thiazole-Linked Polymers

The successful polymerization was confirmed using FTIR spectroscopy, as shown in Figure 12. The dashed line at 3200 cm^{-1} highlights the secondary amine peak of rubeanic acid, the solid line at 1200 cm^{-1} shows its sulfur-carbon peak and the dotted line at 1700 cm^{-1} indicates the aromatic aldehyde peak of TFPPy. The disappearance of all three peaks in the IR spectrum of the polymer indicates that the condensation reactions detailed in Figure 12 was achieved. As shown by the SEM imaging in Figure 12, as a result of pyrene's π-π stacking, DTLP-10 has a nanofiber morphology similar to that observed for BTLP-10.[40] The same was not observed for TzTz-10, which exhibits spherical morphology, likely due to the use of mesitylene as templating agent in the reaction's solvent.[47]

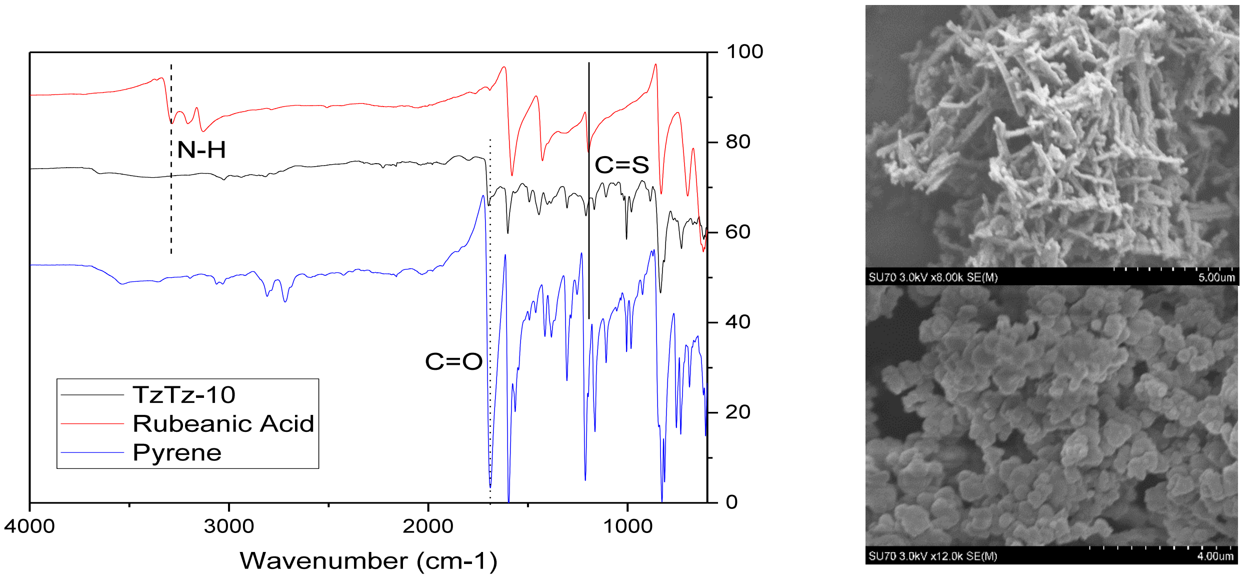


Figure 12. FTIR spectra of the momomers and the synthesized polymer (left). SEM of DTLP-10 (top right) and dTzTz-10 (bottom right).

<u>Porosity and carbon dioxide uptake studies of thiazole linked polymers:</u>

The nitrogen uptake isotherm at 77 K were collected for each polymer and are shown in Figure 13. The isotherms for both polymers show characteristics of type II isotherms. This is indicative of polymers whose pore-size is larger than the adsorbed gas molecule. The size of the pores allows for the formation of a monolayer in which the gas adsorbs on the surface of the polymer, followed by a multilayer where the gas adsorbs on successive layers. The desorption isotherm, shown by hollow markers, follows the adsorption isotherm closely and is indicative of the ability of the polymer to be regenerated. The specific surface area was calculated from the 77 K, N_2 isotherms using the Brunauer-Emmet-Teller model (BET). BTLP-10 showed a surface area of 398 m^2g^{-1} and TzTz-10 had a surface area of 470 m^2g^{-1}. Compared to a reported surface area of 787 m^2g^{-1} for the similarly structured BILP-10, it is likely that there is room for improvement in the synthesis of thiazole-linked polymers.[40] Figure 14 provides the pore size distribution for the polymers as calculated from the BET isotherm, with BTLP-10 showing pores around 13.6 Å and TzTz-10 around 13.1 Å in diameter. The shape of the isotherm, coupled with the pore size distribution, suggests a type I(b) isotherm, indicative of a microporous material with the additional presence of some wider mesopores. The steep increase at low relative pressure is indicative of the molecule-sized micropores having enhanced adsorbent-adsorptive interactions. The slight increase as relative pressure approaches 1 is indicative of the presence of mesopores, which are wide enough to allow additional layers of gaseous molecules to adsorb once the polymer's surface has been completely covered by the initial monolayer.[48]

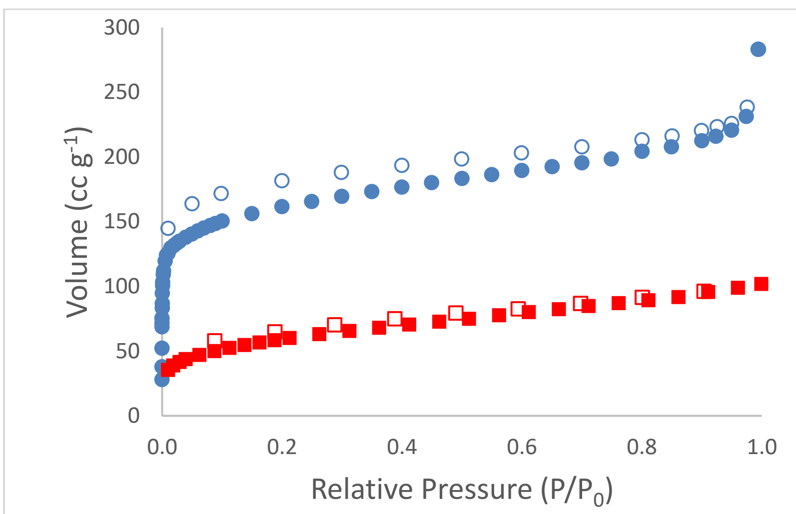


Figure 13. Nitrogen isotherms for BTLP-10 (red squares) and TzTz-10 (blue circles) at 77 K. Adsorption is shown by solid markers and desorption by hollow markers.

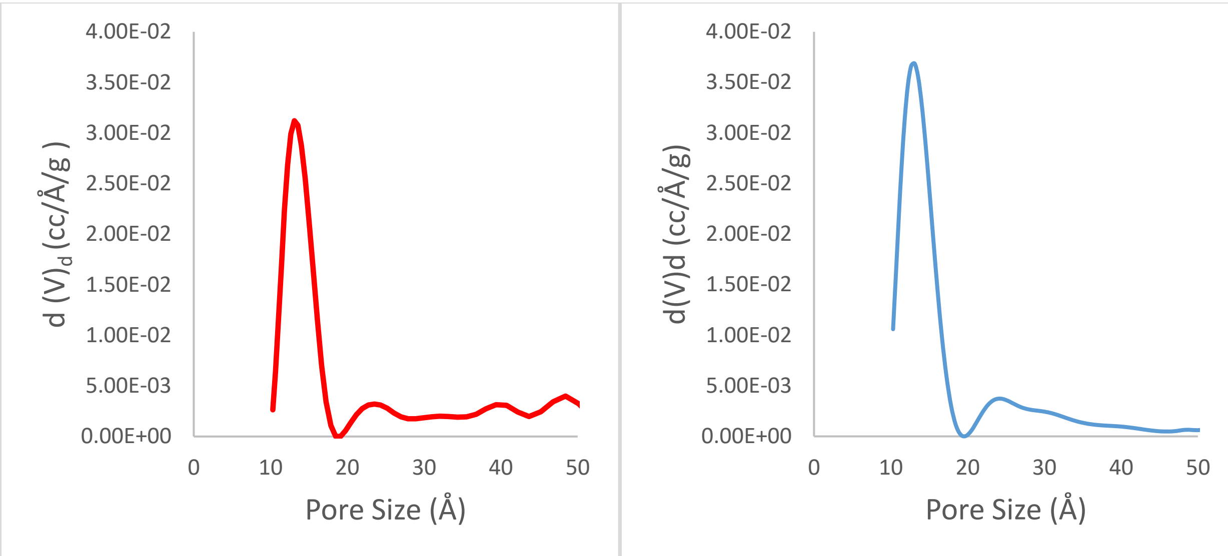


Figure 14. Pore size distribution for BTLP-10 (left) and TzTz-10 (right).

The capacity of both thiazole-linked polymers to capture CO_2 and N_2 is shown in Figure 15. BTLP-10 shows the highest CO_2 uptake at 1 bar with 4.6 mmol g^{-1} at 273 K and 3.3 mmol g^{-1} at 298 K, while TzTz-10 only has an uptake of 2.1 mmol g^{-1} at 273 K and 1.4 mmol g^{-1} at 298 K. BTLP-10 shows slightly larger CO_2 uptake than its benzimidazole equivalent, BILP-10, which captures 4.0 mmol g^{-1} at 273 K and 2.5 mmol g^{-1} at 298 K.[40] It is expected that by optimizing the synthesis of BTLP-10, the uptake could be improved significantly by virtue of improved porosity. TzTz-10's lower uptake on the other hand can be attributed to the loss of the benzene ring component of its linking monomer, which leaves the site of interaction too crowded to properly interact with a large number of CO_2 molecules, and disrupts the configuration of the thiazole dipole moment. Table 9 provides a comparison of the properties of BTLP-10 and TzTz-10 with those of previously reported benzimidazole, benzothiazole and benzoxazole-linked polymers.

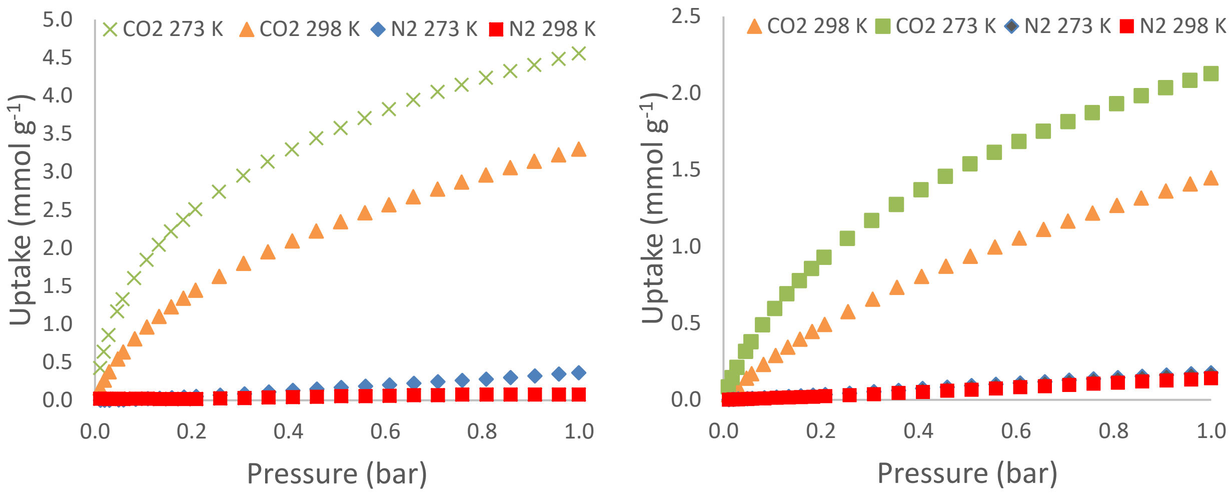


Figure 15. Low pressure uptake of CO_2 and N_2 at 273 K and 298 K by BTLP-10 (left) and TzTz-10 (right).

Table 9. Summary Table.[40,39]

			CO2 uptake at 1 bar (mg g-1)			Selectivity			
	SA ($m2\ g^{-1}$)	PSD (°A)	273 K	298 K	Qst (kj mol^{-1})	CO2/N2 273 K	CO2/N2 298 K	CO2/CH4 273 K	CO2/CH4 298 K
BTLP-10	486	13.6	200	145	29	104	76	17	16
TzTz-10	597	13.1	93	63	21	55	37	6	5
BTLP-4	1011	7.55	190	119	29	41	32	6.9	5.7
BTLP-5	705	7.93	139	87	29	45	42	6.9	5.7
BOLP-4	698	8.68	136	87	34	55	55	9.4	6.9
BOLP-5	759	8.3	129	79	33	54	65	8.8	6.6
BILP-4	1135	6.8	235	158	29	79	32	10	7
BILP-5	599	6.8	128	87	29	95	36	10	6
BILP-10	787	7.6	177	100	18	107	59	14	7
BBO-COF-1	891	13.4	151	92	30	36	35	—	—
BBO-COF-2	1106	18.4	112	70	28	31	31	—	—

Thiazole-Linked Polymers as Sensors for Nitrophenols and Mercury.

The viability of both polymers as sensors for nitrophenol explosives was tested by the analyte-induced quenching of their fluorescence spectra. After suspending each polymer in dichloromethane (0.1 mg ml^{-1}), the photoluminescence spectrum was recorded using an Agilent Cary Eclipse Fluorescence spectrometer. The sample was excited at 340 nm, and an emission peak was observed at 470 nm. Quenching of the emission peak was observed by addition of several aliquots of the nitrophenols and nitrotoluene analytes (10^{-3} M in dichlorometane). Fluorescence quenching for BTLP-10 and TzTz-10 with each analyte are shown in Supporting Figures 2-11.

Figure 16 shows the normalized intensity of the emission spectrum of TzTz-10 decreasing as increasing amounts of TNP are added, as well as the overall quenching for both polymers at 53 ppm of each analyte. Both polymers show excellent sensitivity to the TNP explosive, with fluorescence quenching of 71% and 65% at 53 ppm respectively, outperforming a previously reported TFPPy-based azine-linked polymer which only shows 70% quenching at 70 ppm TNP.[37] The thiazole-linked polymers however also show high sensitivity for the non-explosive species DNP and NP, whereas the azine-linked polymer is highly selective towards TNP alone. While the low selectivity of the thiazole-linked polymers may seem unattractive in a sensor, NP and DNP are byproducts of the synthesis of TNP;[49] BTLP-10 and TzTz-10 may find applicability as a pre-screening sensor capable of detecting nitrophenol explosives in a wider range of scenarios.

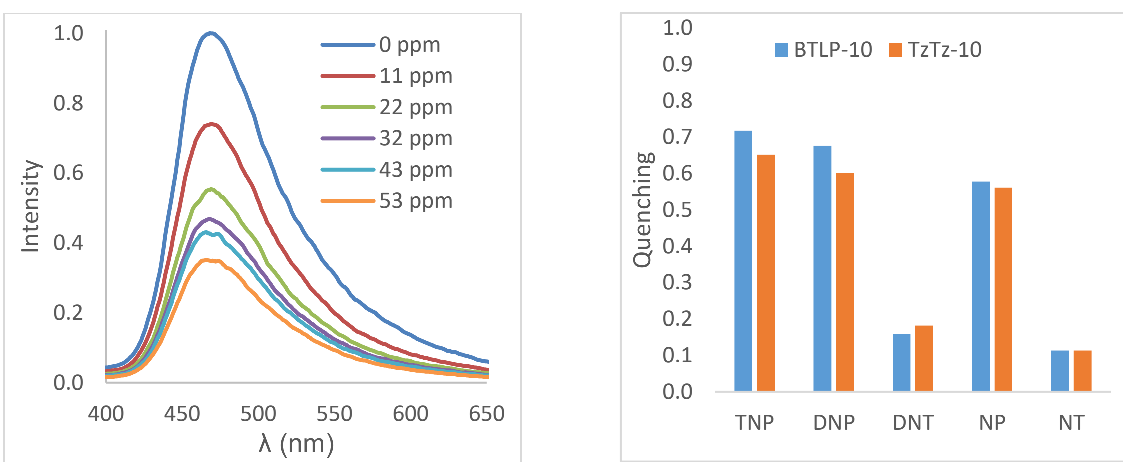


Figure 16. Fluorescence quenching for TzTz-10 with increasing amounts of TNP (left) and quenching at 53 ppm for all species (right).

The sensing of mercury ions was studied by suspending each polymer in acetonitrile (0.1 mg ml^{-1}) and monitoring their real-time fluorescence (excitation 340 nm, emission 470 nm) upon addition of successive aliquots of 10^{-3} M mercury(II) perchlorate in acetonitrile. No fluorescence quenching was observed, even upon addition of large quantities of mercury(II) ions. This is likely due to the relatively weaker nature of the π-donor interaction of sulfur with mercury, which may not be sufficient to delocalized electrons from the polymer's fluorescent pyrene structure in the same way as observed with the more electron-withdrawing nitrophenol moieties. Comparison with other sulfur containing polymers capable of mercury sensing suggests that the thiazole moiety is not ideal for interfacing with Hg^{2+} ions and that the presence of alkyl bonded sulfur is necessary to produce viable sensors.[43,44]

Further analysis tested the polymers' sensitivity to water. Exposure to typical atmospheric conditions (6000 ppm H_2O) showed no discernible quenching, while subsequent addition of nitrophenols quenched the fluorescence as expected, allowing the sensor to be used in humid or aqueous conditions without additional precautions.

The low sensitivity for nitrotoluene species suggests that direct sensing of the explosive trinitrotoluene (TNT) would not be viable. This is further complicated by the fact that TNT exhibits low volatility, making up a minor fraction of its own vapors, and is therefore elusive to most sensors.[50] However the photolysis of TNT, observed in battlefields where unexploded munition is present, leads to the formation of the more volatile nitrophenol species. The lower specificity of BTLP-10 and TzTz-10, when compared with the azine-linked sensor,[37] would therefore make them likely candidates to provide indirect sensing of TNT explosives.[51]

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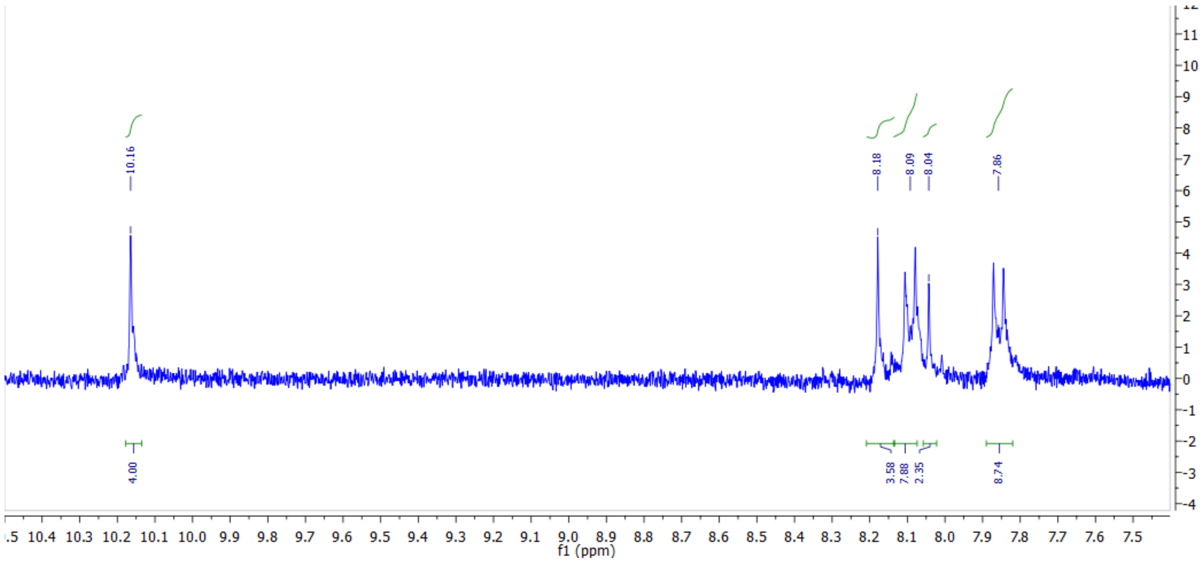
Supporting Information.

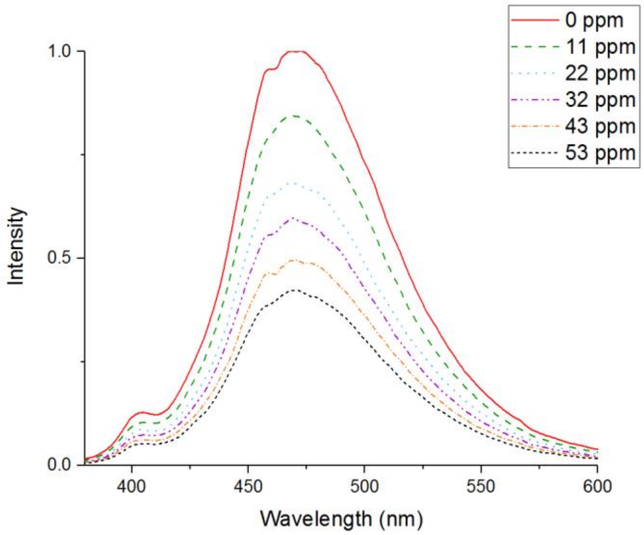
Supporting Table 1. Factor loading for 4 factors.

	Factor Loading			
	1	2	3	4
I feel different from the other people in this class.	-0.296	0.288	0.623	0.553
I often leave the class feeling like I am not as smart as others.	-0.712	0.066	0.414	0.314
I often feel intimidated to participate in the class.	-0.620	0.474	0.189	0.165
I often leave the class feeling like I am the only one who doesnt understand the material well.	-0.705	0.112	0.376	0.348
I worry about getting things wrong in front of the class.	-0.438	0.672	-0.034	0.274
I have generally understood the material as well as the others understand it.	0.782	0.074	-0.097	-0.164
I feel comfortable offering my own ideas in this class.	0.590	-0.499	0.253	-0.033
I feel like its okay to make mistakes in front of others in my class.	0.421	-0.706	0.305	0.066
I feel like I belong in this class.	0.667	-0.205	-0.170	0.378
I feel like its okay to ask dumb questions in the class.	0.344	-0.594	0.305	0.264
I'm confident I can do an excellent job on the assignments and tests in this course.	0.854	0.230	0.134	0.042
I'm certain I can understand the most difficult material presented in the readings for this course.	0.838	0.163	0.187	-0.067
I'm confident I can learn the basic concepts taught in this course.	0.733	0.220	0.004	0.030
I expect to do well in this class.	0.851	0.310	0.057	0.136
I'm certain I can master the skills being taught in this class.	0.865	0.249	0.085	0.063
I'm confident I can understand the most complex material presented by the instructor in this course.	0.859	0.197	0.136	-0.035
I believe I will receive an excellent grade in this class.	0.846	0.331	0.084	0.073
Considering the difficulty of this course, the teacher, and my skills, I think I will do well in this class.	0.869	0.291	0.080	0.116

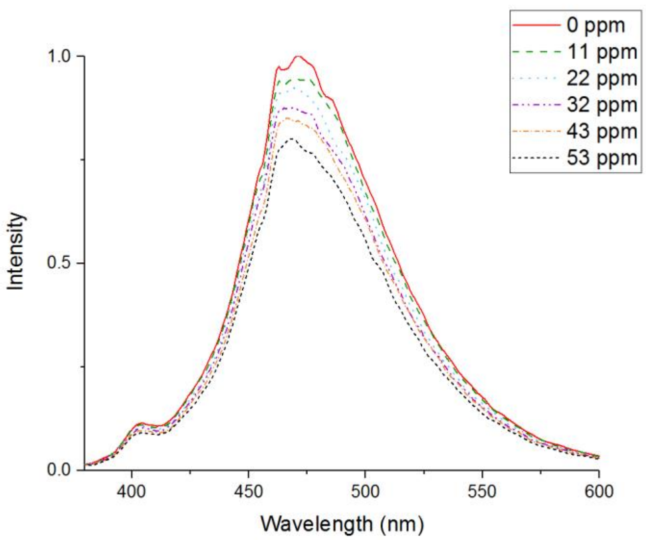


Supporting Figure 1. NMR spectrum of 1,3,6,8-tetrakis(p-formyphenyl)pyrene.

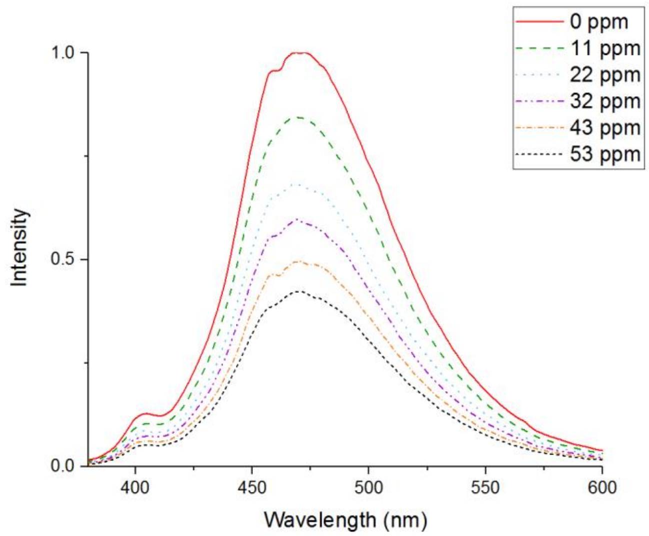
Fluorescence Quenching of BTLP-10



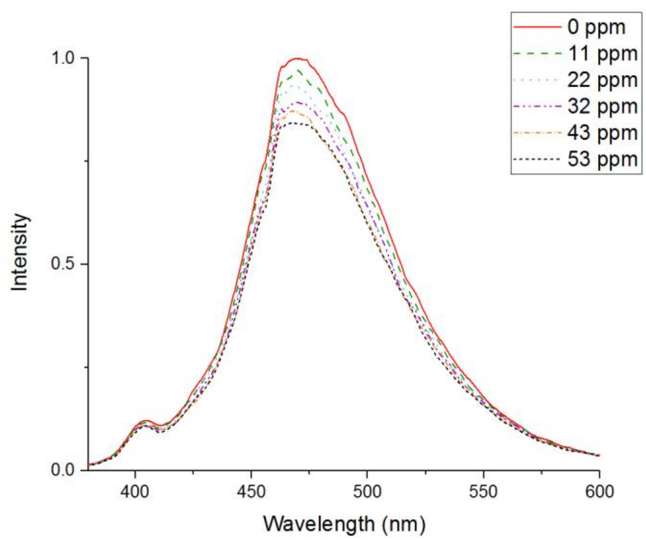
Supporting Figure 2. BTLP-10 quenching by 2-nitrophenol.



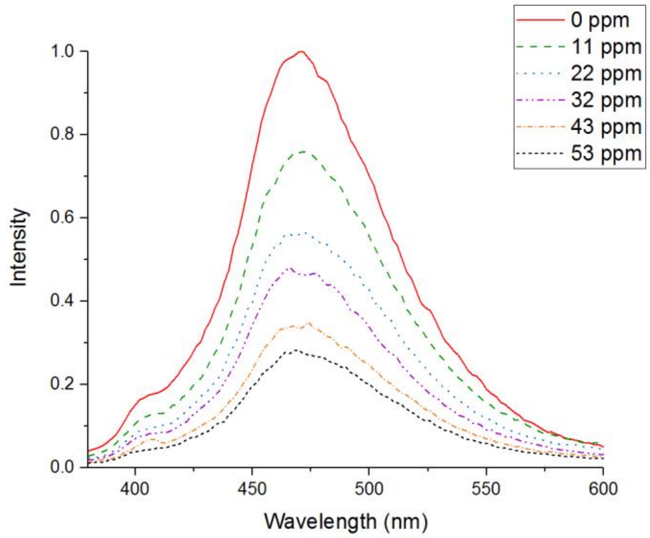
Supporting Figure 3. BTLP-10 quenching by 2-nitrotoluene.



Supporting Figure 4. BTLP-10 quenching by 2,4-dinitrophenol.

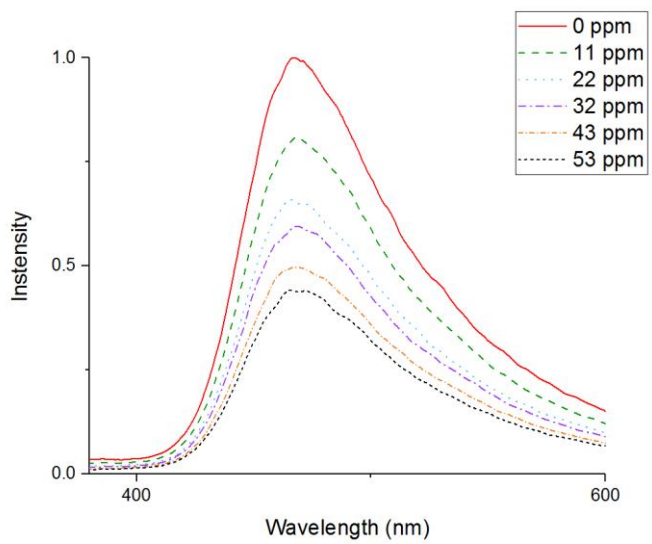


Supporting Figure 5. BTLP-10 quenching by 2,4-dinitrotoluene.

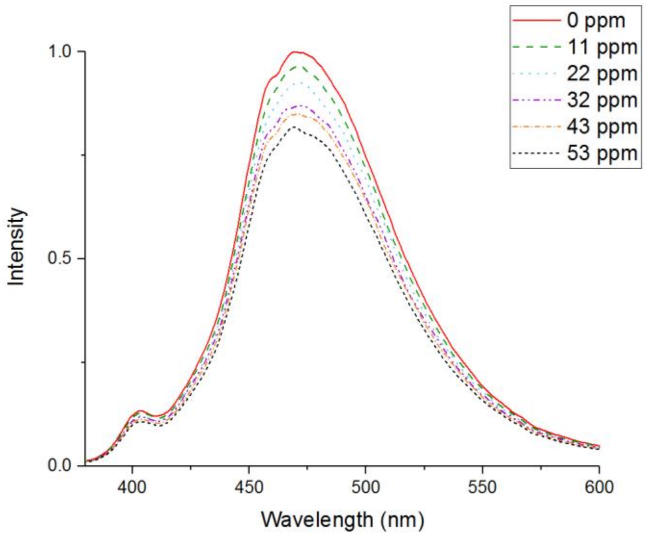


Supporting Figure 6. BTLP-10 quenching by 2,4,6-trinitrophenol.

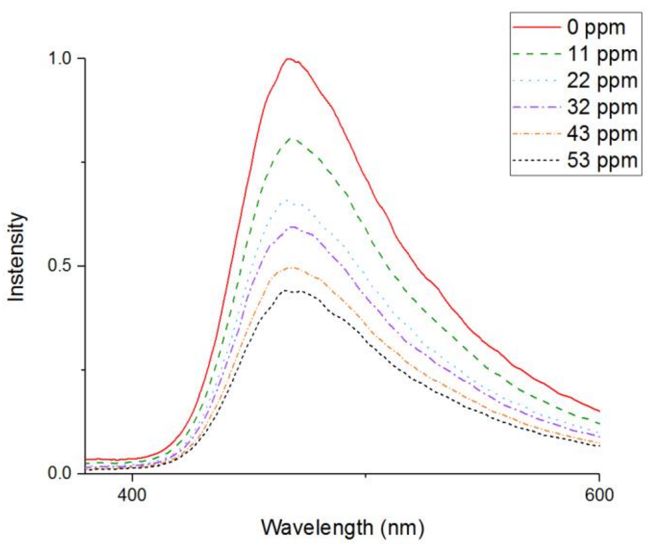
<u>Fluorescence quenching of TzTz-10.</u>



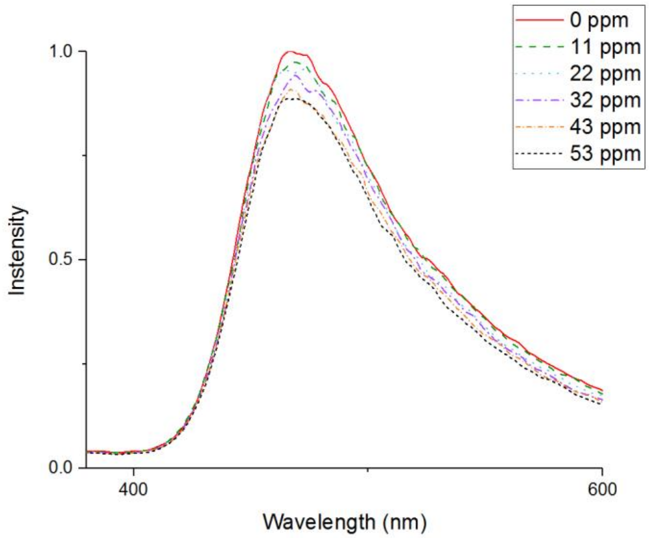
Supporting Figure 7. TzTz-10 quenching by 2-nitrophenol.



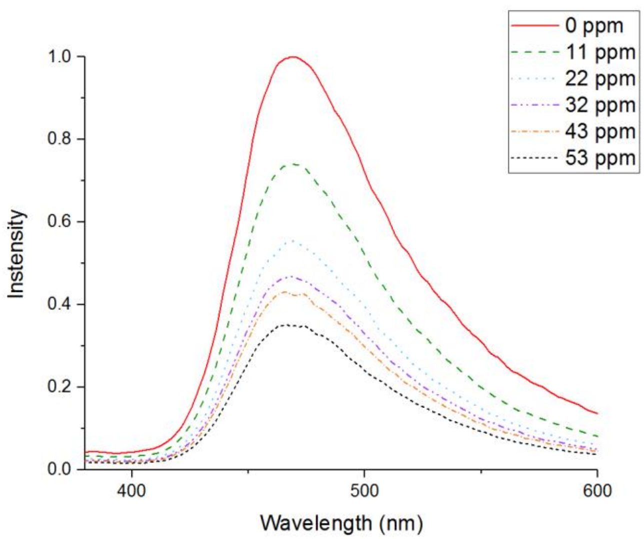
Supporting Figure 8. BTLP-10 quenching by 2-nitrotoluene.



Supporting Figure 9. TzTz-10 quenching by 2,4-dinitrophenol.



Supporting Figure 10. TzTz-10 quenching by 2,4-dinitrotoluene



Supporting Figure 11. TzTz-10 quenching by 2,4,6-trinitrophenol.