

Enhancing Insulated Conjugated Polymer Fluorescence Quenching by Incorporating Dithia[3.3]paracyclophanes

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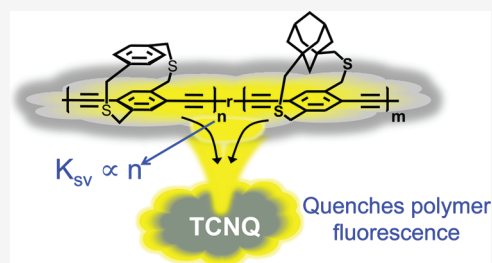
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ABSTRACT: Insulated π -conjugated polymers exhibit enhanced chemical stability, photostability, fluorescence quantum yield, electroluminescence, solubility, and intrachain charge transport. However, insulated polymer fluorescence quenching by acceptor molecules is significantly hampered as the π -face is insulated. Photoinduced charge transfer is one of the key steps in amplified fluorescence quenching sensors and organic solar cells for charge generation. Inspired by the myelin sheath gaps in nerve cell axons, herein, we synthesized a series of insulated random copolymers of adamantanocyclophane with an increasing percentage of dithia[3.3]paracyclophane (PCP) from 5 to 30% to enhance the insulated polymer fluorescence quenching with acceptor molecules.

As the percentage of the dithia[3.3]paracyclophane monomer increases, the copolymers showed an increase in absorption in the red region of the spectrum and also the copolymers' photoluminescence quantum yield reduced. The Stern–Volmer quenching constant of the 30% copolymer is ca. 4.5 times higher than that of the adamantanocyclophane homopolymer. A comparison with the control polymers indicated that the through-space-coupled interactions in PCP could be a plausible reason for the enhanced fluorescence quenching in copolymers in addition to the reduced steric hindrance by PCP. The developed copolymers combine the advantages of polymer insulation without significantly sacrificing the photoinduced charge transfer, which will help further their applicability as amplified fluorescence quenching sensors and in organic solar cells.



INTRODUCTION

Sheathing a π -conjugated polymer backbone insulates the conjugated backbone and enhances its chemical stability, photostability, fluorescence quantum yield, electroluminescence, and intrachain charge transport.^{1–18} In addition, these insulated conjugated polymers also enable nonlinear optical properties.^{2,4} For example, conjugated polymers do not typically form self-free-standing films like conventional plastics; however, Takeuchi and Sugiyasu have shown that doubly strapped conjugated polymers are thermoformable like conventional plastics.¹⁵ Recently, Bronstein and co-workers have shown that doubly strapped π -conjugated polymers hinder interchain interactions and reduce the gap between the solution and solid-state quantum yields.^{10,13,14} Instead of alkyl straps, chemically diverse straps can be used to generate novel functional polymers; for example, Giovannitti and co-workers have used ethylene oxide straps instead of alkyl straps to selectively detect sodium and potassium ions in both solution and solid states.¹⁵ The Smith group has used aryl straps based on sterically encumbered *m*-terphenyl instead of alkyl straps to semi-insulate π -conjugated polymers.^{11,12} The aryl straps also reduce interchain interactions in the solid state and enhance the sensory response toward nitroaromatic vapors similar to pentiptycene polymers derived by the Swager^{19,20} group. Swager's pentiptycene polymers, although not strapped polymers, reduce the interchain interactions between the polymers in thin films and generate a porous structure, which

enhances the diffusivity of analytes in the thin films and therefore the sensory response of polymers toward electron-deficient analytes.^{19,20} Thus, the straps help to overcome the limitations of conjugated polymers and render new properties in few cases. Because of these reasons, the research in this direction, although limited for now, has been increasing recently. Therefore, multiple strategies have been devised to insulate π -conjugated polymer backbones, including molecular sheathing by cyclodextrins and the use of alkyl chains and cycloalkyl straps.^{2,6–8,10,11,15,16}

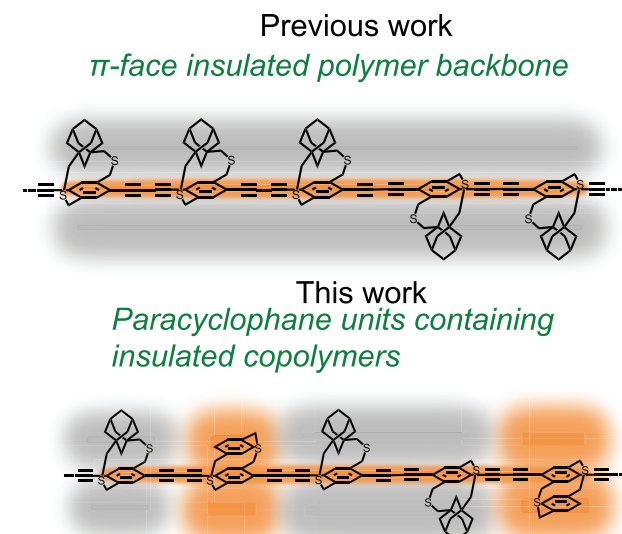
Recently, we have shown that the cycloalkyl straps efficiently block the π -face of the repeat unit and render soluble polymers with higher solubility limits than the conventional π -conjugated polymers that have pendant solubilizing chains.^{6,18} We have also shown that the size of the strap is useful to control the polymer solubility by demonstrating that solubility increased as the height of the cycloalkyl group increased.⁶ In addition to imparting solubility, the strapped polymers also render the advantage of selectively blocking the π -face of the

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repeat unit unlike the cyclodextrin-encapsulated insulated polymers (Scheme 1).^{6–8} This allows the strapped monomers

Scheme 1. Paracyclophane Units Incorporated along the Insulated Polymer Backbone Enhance the Insulated Polymer's Photoinduced Charge Transfer to Acceptor Molecules and Hence the Polymer's Fluorescence Quenching



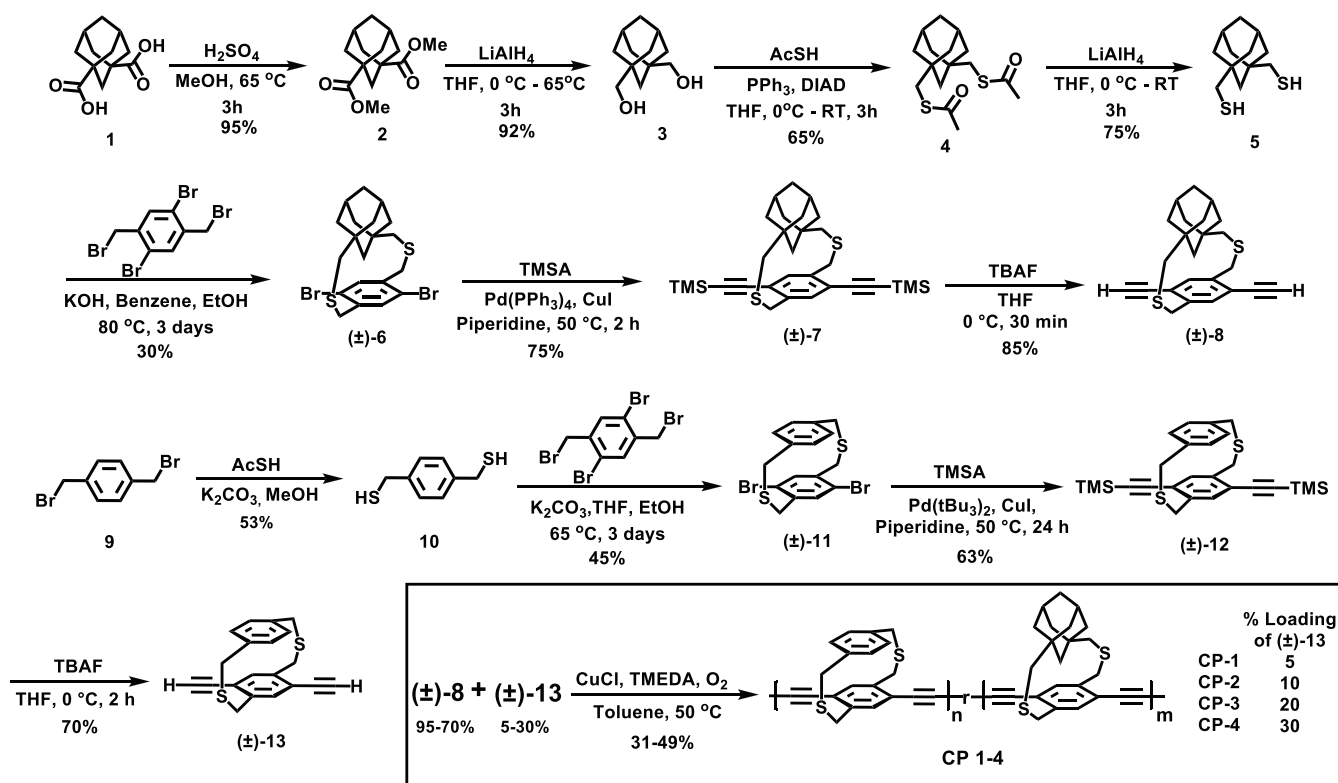
to fuse along the polymer backbone to generate soluble nanoribbon polymers without pendant solubilizing chains.^{7,8} However, insulation of the π -face of the conjugated polymer reduces the fluorescence quenching by a tetracyanoquinodi-

methane (TCNQ) acceptor. The photoluminescence quenching of a donor polymer by an acceptor is one of the key steps in charge generation in organic solar cells and amplified fluorescence quenching sensors. Therefore, even though the insulated polymers have several advantages, charge transfer to acceptor molecules and other polymer chains is significantly hampered as the π -face is insulated.^{2,4} Insulated polymers that combine the advantages of insulation without significantly sacrificing the photoinduced charge transfer will help further their applicability as amplified fluorescence quenching sensors and in organic solar cells.

Insulated conjugated polymers are not unique to the synthetic material world as this structural design is observed in nature in nerve cells as well. Nerve cell axons are coaxially covered by myelin, an insulating sheath, to increase the transport rate of electrical impulses along the axon.^{21–23} Nature cleverly does not insulate the axon continuously but leaves periodic gaps known as myelin sheath gaps or nodes of Ranvier. These gaps mostly contain ion channels and are exposed to extracellular space, which are useful to regenerate the action potential. The insulated axon structure with myelin sheath gaps serves as a good inspiration for overcoming the challenges mentioned above in the case of synthetic insulated conjugated polymers and generating the next generation of insulated π -conjugated polymers.

Inspired by this, herein, to enhance the insulated π -conjugated polymer fluorescence quenching by acceptor molecules, dithia[3.3] paracyclophanes (PCPs) are incorporated along an insulated adamantanocyclophane polymer (Scheme 1). Unlike an adamantanocyclophane (ACP), [m.n]cyclophanes contain two phenyl rings, and both the phenyl rings interact via through-space π – π interactions called transannular π – π interactions.^{24–28} It has been shown that the

Scheme 2. Synthesis of Copolymers (CP-1–4)



transannular π – π interactions enable the charge-transfer complexes of bilayer and multilayer [3.3]cyclophanes with the tetracyanoethylene acceptor as well as interchain charge and energy transfer.^{24–27,29–32}

The PCP units are randomly incorporated along the adamantanocyclophane polymer, resulting in random cyclophane copolymers (CPs). We hypothesize that PCPs will act similar to the myelin sheath gap node in the axons and enhance the photoinduced charge transfer with acceptor molecules. In order to understand the role of the PCP units, four different random copolymers of ACP and PCP are synthesized with the systematically increasing fraction of PCP from 5, 10, 20, to 30% (CP-1 to CP-4). UV–vis absorption, emission, and fluorescence quenching properties of the copolymers are compared with the control polymers. The through-space-coupled phenyl rings in the PCP units have significantly altered the UV–vis absorption and emission properties of the copolymers and indicate that PCP acts as an acceptor in the copolymers. As the percentage of PCP increases, the fluorescence of the copolymers is quenched more effectively by the TCNQ acceptor. The K_{sv} value of CP-4 with 30% PCP units is ca. 4.5 times higher than that of the ACP homopolymer. The reduced steric hindrance due to the PCP unit compared to the ACP unit allows TCNQ to easily access the polymer backbone and quench the emission. A comparison with the copolymers' K_{sv} value indicated that, in addition to sterics, the through-space interactions in PCP could be a plausible reason for enhanced quenching.

RESULTS AND DISCUSSION

($\pm$)-Diethynyl adamantanocyclophane monomer (($\pm$)-8) was synthesized from 1,3-adamantane dicarboxylic acid (**1**) following our previously reported protocol (Scheme 2).⁶ Compound **1** was esterified and reduced to generate 1,3-adamantane dimethanol (**3**). Compound **3** was converted into a thioester and then reduced to generate 1,3-adamantane dimethanethiol (**5**). Compound **5** was reacted with 1,4-dibromo-2,5-bis(bromomethyl)benzene under high-dilution conditions to yield a racemic mixture of ($\pm$)-dibromo adamantanocyclophane (**6**). Compound **6** is obtained as a racemic mixture due to planar chirality. Sonogashira coupling of compound ($\pm$)-**6** with trimethylsilyl (TMS)acetylene followed by desilylation resulted in the ACP monomer ($\pm$)-**8**. ($\pm$)-Diethynyl dithia[3.3] paracyclophane monomer (**13**) was synthesized from 1,4-bis(bromomethyl)benzene (**9**), following the reported synthetic protocols.³³ Compound **9** was reacted with thioacetic acid in the presence of potassium carbonate in methanol to generate 1,4-bis(thiomethanol)-benzene (**10**). Compound **10** and 1,4-dibromo-2,5-bis(bromomethyl)benzene were reacted under high-dilution conditions for 3 days to generate ($\pm$)-dibromo dithia[3.3]-paracyclophane (($\pm$)-**11**). Sonogashira coupling of compound ($\pm$)-**11** with TMS acetylene followed by desilylation resulted in the PCP monomer ($\pm$)-**13**.

Random copolymers of the ACP monomer (**8**) and PCP monomer (**13**) were synthesized, following the similar Glaser–Hay polymerization protocol used for the ACP homopolymer synthesis.⁶ In a typical procedure, both the monomers (($\pm$)-**8** and ($\pm$)-**13**) were reacted in the presence of copper (I) chloride and tetramethylethylenediamine (TMEDA) in toluene in the presence of air at 50 °C (Scheme 2). All of the generated copolymers are atactic in nature, that is, there is no control over the orientation of the cyclophane units along

the polymer backbone, as a racemic mixture of monomers was used to synthesize the copolymers. The monomer feed ratio was adjusted for the desired amount of PCP in the copolymer backbone (5, 10, 20, and 30%) (Table 1). The copolymers

Table 1. Structural Details of Copolymers

copolymer	PCP feed ratio	M_n (kDa)	PDI	percent PCP incorporated
CP-1	5	13.5	2.58	4.7
CP-2	10	12.1	2.56	9.9
CP-3	20	11.2	1.77	19.7
CP-4	30	11.0	2.49	29.2

with more than 30% of the PCP units are not soluble enough to grow into the desired molecular weight. The polymerization time was adjusted to achieve similar molecular weights for all the copolymers. Having copolymers of similar molecular weight eliminates the effect of molecular weight when comparing the copolymers' properties. The polymerization reaction mixture was added to methanol to stop the polymerization, and the resultant polymer precipitate was purified by soxhlation using methanol and chloroform. The chloroform solution was concentrated under a vacuum and reprecipitated in ether and filtered. The resultant polymer was dried and used for further characterization. The copolymer molecular weights were determined using gel permeation chromatography (tetrahydrofuran as the eluent) against polystyrene standards. The number average molecular weights of the copolymers are in the range of 11–14 kDa (Table 1 and Figure S1). All the copolymers are soluble in chloroform and tetrahydrofuran. However, only the copolymers having a lower percentage of PCP (CP-1–2) are soluble in dichloromethane, indicating that the PCP units promote interchain interactions.

The percent inclusion of PCP units into the copolymers was determined using ¹H NMR analysis (Figure 1 and Table 1). Based on the ¹H NMR data of the ACP homopolymer,⁶ the two peaks downfield from the CDCl₃ residual solvent peak (δ = 7.26 ppm) in the copolymer correspond to the aryl peaks from ACP. A good (1:1) correlation between the aryl peaks and highly shielded adamantane methylene protons further confirms that these two aryl peaks are from ACP. The aryl peak upfield from the CDCl₃ residual solvent peak corresponds to the four-aryl protons of the through-space-coupled phenyl ring of PCP. The two-aryl protons corresponding to the diethynyl phenyl ring of PCP are buried inside the CDCl₃ solvent residual peak. To confirm this, the ¹H NMR data of CP-2 (10% PCP) was recorded in CD₂Cl₂ and is shown in Figure 1. Indeed, there is an aryl peak around 7.24 ppm corresponding to the protons of the diethynyl phenyl ring of PCP. The aryl protons corresponding to the through-space-coupled phenyl ring of PCP are observed at 7.13 and 7.08 ppm. The ratio of integration of the protons corresponding to the diethynyl phenyl ring of PCP and the through-space-coupled phenyl peaks of PCP matches well with the structure. As CP-3 and CP-4 are sparingly soluble in CD₂Cl₂, the ¹H NMR data of all the copolymers are recorded in CDCl₃ and compared. The stacked ¹H NMR spectra of the copolymers in Figure 1 demonstrate the growth of the PCP peak at 7.1 ppm with an increasing feed ratio of the PCP monomer in the polymerization. The percentage of PCP units in the copolymers (Table 1) is determined by the ratio of the integration of the through-space-coupled phenyl peaks in PCP to the aryl peaks in ACP.

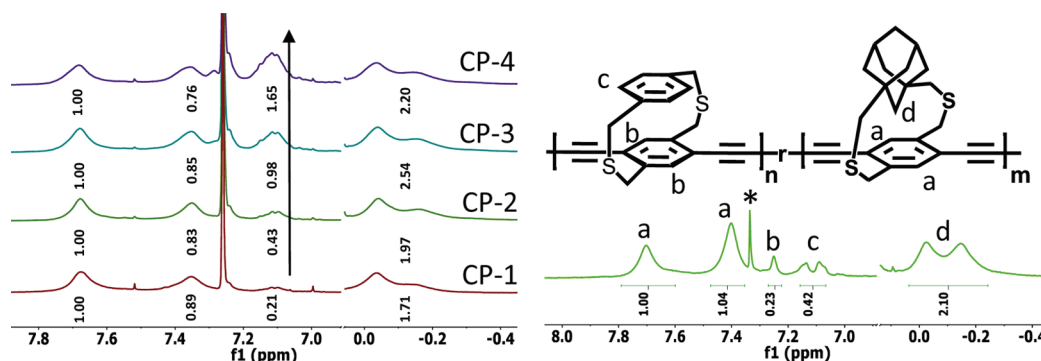


Figure 1. (Left) ^1H NMR spectra of copolymers in CDCl_3 ; (right) ^1H NMR spectra of CP-2 in CD_2Cl_2 ; the sharp peak at 7.3 ppm (*) is from chloroform.

Based on this analysis, there is a one-to-one correlation between the feed ratio of PCP (f_1) to its incorporation (F_1) into the copolymer (Figure 2). Based on the Mayo–Lewis

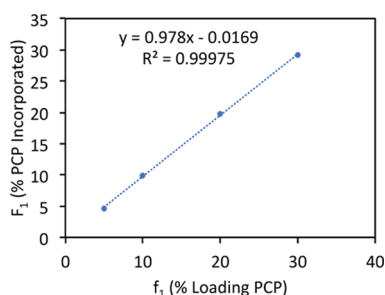


Figure 2. Mayo–Lewis plot of the PCP copolymer composition.

model for copolymer composition (eq 1),^{34–36} it is indicated that the reactivities of both the monomers are equal to unity and the resultant copolymers are random copolymers.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (1)$$

The equal reactivities of both the ACP (r_2) and PCP (r_1) monomers indicate that the transannular π – π interactions in PCP have no effect on the reactivity of acetylenes in the PCP monomer under Glaser–Hay polymerization conditions.

To understand the impact of incorporating the PCP units along the polymer backbone, the UV–vis absorption and emission spectra of the copolymers were recorded in chloroform. The samples are prepared based on the repeat

unit molecular weight. The absorption spectra of the copolymers are significantly similar to each other, with the absorption maximum around ca. 420 nm. The absorption spectra (Figures 3 and S2) of copolymers differ in the higher wavelength (>450 nm) and lower wavelength (<300 nm) regions. The absorbance of peaks below 300 nm and above 450 nm increases as the percentage of the PCP monomer increases. The optical properties of CP-4 are compared with the optical properties of two control polymers, adamantanocyclophane homopolymer (ACP homopolymer) and control-CP, to further gain insights into the role of the through-space-conjugated phenyl ring in the PCP repeat unit (Figure 4). The ACP homopolymer contains only ACP repeat units, whereas the control-CP contains an equimolar mixture of both adamantocyclophane and cyclohexanocyclophane repeat units. Cyclohexanocyclophane contains the cyclohexyl group instead of the phenyl ring as part of the cyclophane. Cyclohexane is the saturated version of the phenyl ring, so the difference in the optical properties between the control-CP and CP-4 can be attributed to the through-space-conjugated phenyl ring in CP-4, that is, transannular interactions. The synthesis and optical properties of the ACP homopolymer and the control-CP have been reported by us previously.⁶ For easy comparison between these polymers, the optical data of the ACP homopolymer and the control-CP polymer are plotted along with those of CP-4 in Figure 4. The absorption spectrum (Figure 4) of CP-4 is similar to that of the ACP homopolymer except for the regions below 300 nm and above 450 nm. The intensity of the peaks below 300 nm is higher for CP-4 compared to the control polymers. The additional phenyl ring, that is, the through-space-conjugated phenyl ring, might be a

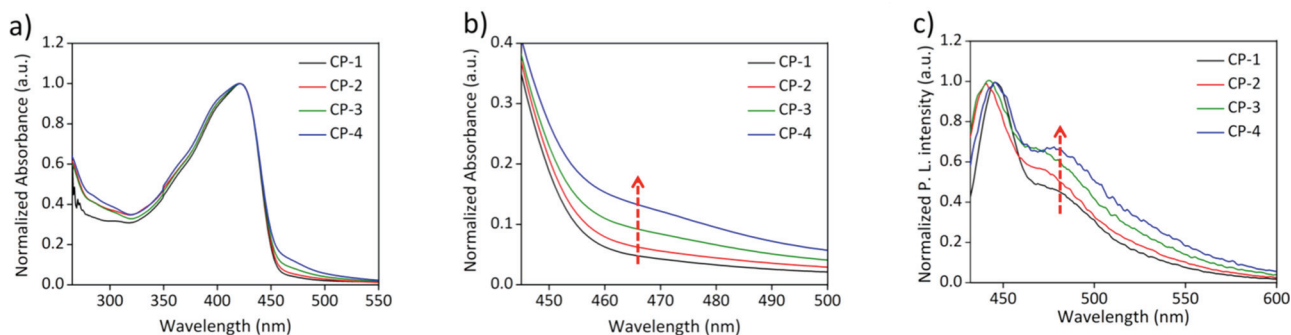


Figure 3. (a) UV–vis absorption spectra of copolymers in chloroform; (b) zoomed tail-end region of the UV–vis absorption spectra of the copolymers; and (c) fluorescence spectra of the copolymers in chloroform.

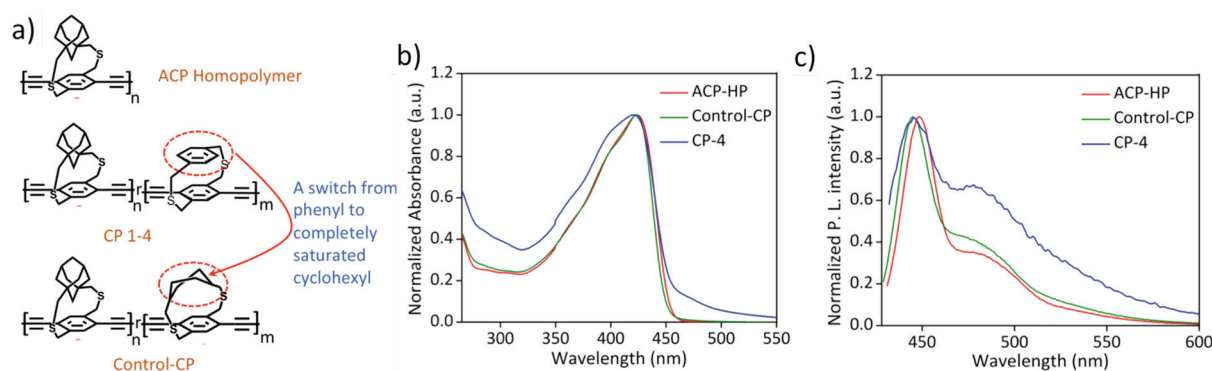


Figure 4. (a) Comparison of control polymer structures; comparison of (b) UV–vis absorption spectra and (c) emission spectra of CP-4 with control polymers (ACP homopolymer and control-CP).

Table 2. Comprehensive Optical Properties of Copolymers

polymer	%PCP	$\lambda_{\text{max}}^{\text{abs}}$ (nm) in CHCl_3	$\lambda_{\text{max}}^{\text{abs}}$ (nm) in thin film	molar extinction coefficient ($\times 10^3$) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)		$\lambda_{\text{max}}^{\text{em}}$ (nm) in CHCl_3	I_{480}/I_{448}	quantum yield ^a	K_{sv} ($\times 10^3$) (M^{-1})
				@ $\lambda_{\text{max}}^{\text{abs}}$	@472 nm				
CP-1	5%	422	421	28.3	1.3	448, 480	46%	0.11	35 ± 4
CP-2	10%	421	424	29.5	1.45	449, 480	53%	0.10	42 ± 3
CP-3	20%	421	420	28.7	1.95	448, 478	62%	0.08	44 ± 3
CP-4	30%	420	418	23.8	2.4	446, 478	67%	0.06	58 ± 6

^aRelative to perylene in ethanol.

possible reason for the higher intensity of peaks below 300 nm in CP-4. CP-4 has a higher absorbance near the tail end of the spectrum (between 455 and 500 nm) compared to the ACP homopolymer and the control-CP. This indicates that the appearance of a new peak near the tail end of the absorption spectrum is due to the PCP monomers. The increase in the absorbance of the peak between 455 and 500 nm as the percentage of the PCP monomer increases could be due to either the aggregation of polymers in solution and/or intramolecular charge transfer between the ACP and PCP units. In order to determine the root cause of this, the concentration-dependent UV–vis absorption spectra of the copolymers are recorded at low concentrations (13–50 μM) in chloroform. The concentrations of the copolymers are determined using the corrected repeat unit molecular weight that includes the percentage of the ACP and the PCP repeat units. The intensity of the red region of the spectrum increased linearly with concentration for all the copolymers (Figures S3–S6). Molar absorptivities of the copolymers at 472 nm (corresponding to the red region of the spectrum) and at the absorption maximum are determined (Table 2) using the Beer–Lamberts law. The molar absorptivities of copolymers at 472 nm increases from 1300 to $2400 \text{ M}^{-1} \text{cm}^{-1}$ as the percentage of the PCP repeat units increases from 5 to 30%. However, the molar absorptivities at the absorption maximum showed no correlation with the percentage of the PCP repeat units. Dynamic light scattering measurements on the copolymer samples close to the UV–vis sample concentrations showed no clear indications of aggregates in the solution. Thus, the presence of an absorption peak at 472 nm even at a low copolymer concentration, the linear correlation between the absorbance at 472 nm and the copolymer concentration, and the increase in the molar absorptivity of the copolymers with an increase in the PCP repeat units indicate that the absorption near the tail end of the spectrum is due to the

intramolecular charge transfer between the ACP and the PCP units. In the case of conventional π -conjugated alternating copolymers of PCP, it has been shown that the PCP unit acts as an acceptor and quenches the emission.^{37,38} In the copolymers reported here also, the PCP unit acts as an acceptor and the ACP unit acts as a donor. Frontier molecular orbitals (FMOs) of a model trimer (ACP–PCP–ACP) are calculated using DFT-B3LYP/6-31G* calculations and are shown in Figure 5 (Table S1). There is some electron density

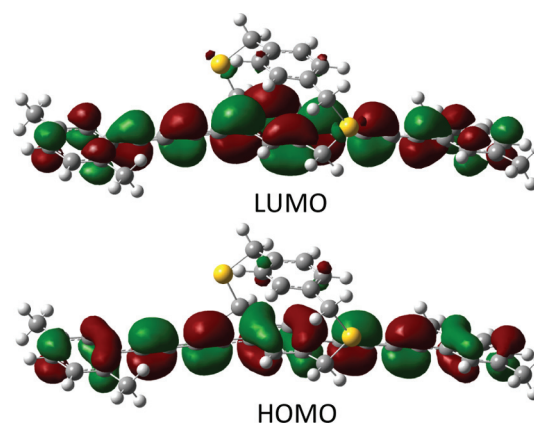


Figure 5. Frontier molecular orbitals of a model trimer: ACP–PCP–ACP; xylene is used instead of adamantanocyclophane.

located on the through-space-conjugated phenyl ring of the PCP units in both the FMOs, suggesting that it has a role in the optical properties of the copolymers. The absorption spectra of copolymer thin films are recorded and are shown in Figure S7. The thin-film absorption spectra of copolymers are similar to that of the solution state spectra. A negligible shift in the absorption maximum from the solution to thin films is also

observed in PCP containing alternating copolymers^{37,38} and is not unique to the CPs synthesized in this work.

The emission spectra of the random CPs in solution are shown in Figures 3 and S8. All the CPs show an emission maximum at ca. 448 nm and a shoulder at 480 nm. The emission capability of the copolymers, that is, the intensity of the emission maximum, reduces with the increasing percentage of the PCP monomer (Figure S8). Indeed, the photoluminescence quantum yield reduces from 14 to 6% with the increasing percentage of the PCP monomer from 0 to 30% (Table 2 and Figures S9–S13). Interestingly, the ratio of the intensity of the shoulder (480 nm) peak to the emission maximum (448 nm) increases from 35 to 67% as the percentage of the PCP units increases from 0 to 30% (Table 2). This indicates that the PCP units show more impact on the emission process corresponding to the emission maximum (ca. 448 nm peak) compared to the shoulder peak (ca. 480 nm). The emission spectrum of CP-4 is compared with that of the ACP homopolymer and the control-CP (Figure 4). The ratio of the intensity of the shoulder (480 nm) peak to the emission maximum (448 nm) is 34 and 40% for the ACP homopolymer and the control-CP respectively. Even though the control-CP contains 50% of the cyclohexanocyclophane comonomer, the intensity ratio (40%) is significantly lower than that of CP-4 (67%) and much closer to that of the ACP homopolymer (34%). This clearly indicates that the through-space-conjugated phenyl ring has an impact on the emission properties of the copolymers. As mentioned above, the PCP units act as acceptors and contribute to the partial quenching of the copolymers' fluorescence, resulting in a reduction of the copolymers' emission intensity with an increasing percentage of the PCP units.

Fluorescence quenching studies of the copolymers with a TCNQ acceptor are done to determine the role of PCP in the copolymers. The fluorescence quenching studies of the CPs with a TCNQ acceptor were carried out and compared with that of the ACP homopolymer and the control-CP (Figure 6). The fluorescence intensity of all the copolymers reduced as the TCNQ concentration increased, and the reduction in intensity followed a concave-upward curvature of the Stern–Volmer

(SV) plot. In general, the nonlinear Stern–Volmer plot is due to simultaneous dynamic and static quenching.^{39,40} The data were fitted to a reported nonlinear SV equation⁴¹ to obtain the SV constant (K_{sv}) (Figures S14–S17). K_{sv} increased as the percentage of the PCP units increased in the CPs (Table 2). Moreover, K_{sv} of CP-4 with 30% PCP units is 4.5 times that of the ACP homopolymer.

In order to determine the role of the through-space-conjugated phenyl ring and hence the PCP monomer on the increase in K_{sv} , the K_{sv} values of the ACP homopolymer (K_{sv} : $13 \times 10^3 \text{ M}^{-1}$) and the control-CP (K_{sv} : $17 \times 10^3 \text{ M}^{-1}$) are compared with that of CP-4.⁶ The increase in the K_{sv} value from the ACP homopolymer to the control-CP was attributed to the smaller height/size of the cyclohexanocyclophane unit.⁶ The butadiyne linkers provide enough space between the repeat units and allow the repeat units to rotate freely around the polymer axis. Hence, the polymer structure resembles a cylinder where the cycloalkyl groups or the through-space-coupled phenyl ring form a sheath around the polymer backbone (Scheme 1). The diameter of the cylinder is determined by the height of the repeat unit. The height of cyclohexanocyclophane is lower than that of adamantanocyclophane by 1.3 Å (reduction in height of 18%).⁶ This allows the TCNQ molecules to approach the control-CP polymer backbone relatively closely compared to the ACP homopolymer backbone, resulting in enhanced fluorescence quenching by 30%. Based on a similar analysis, the PCP unit is smaller in height compared to the ACP unit by 3.52 Å (reduction in height of 48%). The K_{sv} value of CP-4 is enhanced by 346%. Hence, the reduction in the repeat unit height has a significant contribution in increasing the K_{sv} value. However, the increase in the percentage of K_{sv} with the drop in the repeat unit height is dramatic in the case of CP-4 compared to the control-CP. Thus, in addition to steric reasons, the through-space-conjugated phenyl ring also might play a significant role in increasing the sensing capability of CP-4. The through-space interactions in PCP could be a plausible reason for the enhanced photoinduced charge transfer from the polymer backbone to the TCNQ molecule.

CONCLUSIONS

To summarize, a series of π -face-insulated polymers with an increasing amount of dithia[3.3]paracyclophane have been synthesized, and their optical properties have been studied. The similar reactivity of adamantanocyclophane (insulated monomer) and dithia[3.3]paracyclophane resulted in the random incorporation of PCP units along the polymer backbone. The PCP unit acts as an acceptor, resulting in an intramolecular charge-transfer peak in the UV–vis absorption spectra of copolymers and a reduction in the photoluminescence quantum yield of the copolymers. The smaller size of the PCP units allowed the TCNQ acceptor molecules to approach the polymer backbone closely, resulting in an enhanced fluorescence emission quenching of the insulated polymer backbone. The K_{sv} value of random CPs increased as the amount of PCP units increased. The K_{sv} value of the 30% CP is ca. 4.5 times that of the adamantanocyclophane homopolymer. A comparison of the K_{sv} values of the control polymers with that of the copolymers indicated that the through-space interactions of PCP could also play a role, in addition to the reduced steric hindrance, for the enhancement of K_{sv} . Thus, the incorporation of the PCP units along the π -face-insulated polymer backbone enhances the efficiency of

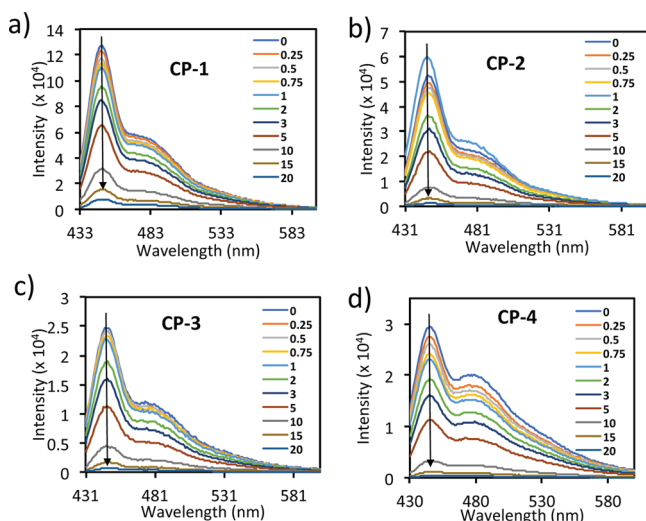


Figure 6. Fluorescence emission quenching of copolymers upon the addition of TCNQ. The mole ratio of TCNQ to the polymer repeat unit is shown in the legend.

photoinduced electron transfer to acceptor molecules. The through-space interactions in the PCP units are also expected to facilitate interchain charge transfer/transport. Thus, the developed strategy will help to generate insulated polymers that combine the advantages of insulation without significantly sacrificing the charge and energy transport across the bulk material, which furthers their applicability in many electronic and optoelectronic devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c00136>.

Synthesis, characterization details, and characterization of polymers (PDF)

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Notes

The authors declare no competing financial interest.

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