INTRODUCTION

Covalent organic polymers (COPs) have gained increased attention during recent years due to their high porosity, low mass density, tunable structural properties, and more importantly, their unique physicochemical stability arising from the entirely covalently bonded networks. COPs have distinguished themselves as a new class of materials for potential applications in catalysis, gas storage and separation, chemosensing, and in drug delivery. In particular, the increasing concentration of carbon dioxide in the environment due to anthropogenic activities poses challenges to design new absorbent materials toward equipment. Although porous metal-organic frameworks (MOFs) possess high crystallinity and porosity for its sensing and gas adsorption properties, MOFs are also harmful to human health and the environment. The amine solution employed in industry for the capture and storage of CO₂ is an alternative way to enhance CO₂/N₂ selectivity and loading capacity. Because of their tunable organic framework, COPs can be manipulated to carry optically active functionalities. For example, material chemists in the last few years have started designing π-conjugated luminescent materials for use in various applications such as light harvesting, light-emitting diodes, chemosensors, etc. One such chemosensing application is the sensing of polynitroaromatic compounds (PNACs). Devices and explosives derived from PNACs pose a great threat to national security in an era of rising terrorism-related activities and are also harmful to human health and the environment. Several analytical methodologies have been developed for sensing nitroaromatic explosives. However, many are found to be expensive and cumbersome. On the contrary, fluorescent-based probes offer high sensitivity, portability, and real-time monitoring at low cost. The best reported chemosensors for this purpose are the π-conjugated systems, which utilize perturbation in fluorescence as the signaling mechanism.

Bulky Isopropyl Group Loaded Tetraaryl Pyrene Based Azo-Linked Covalent Organic Polymer for Nitroaromatics Sensing and CO₂ Adsorption

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ABSTRACT: An azo-linked covalent organic polymer, Py-azo-COP, was synthesized by employing a highly blue-fluorescent pyrene derivative that is multiply substituted with bulky isopropyl groups. Py-azo-COP was investigated for its sensing and gas adsorption properties. Py-azo-COP shows selective sensing toward the electron-deficient polynitroaromatic compound picric acid among the many other competing analogs that were investigated. Apart from its chemosensing ability, Py-azo-COP (surface area 700 m² g⁻¹) exhibits moderate selectivity toward adsorption of CO₂ and stores up to 8.5 wt % of CO₂ at 1 bar and 18.2 wt % at 15.5 bar at 273 K, although this is limited due to the electron-poor N=N linkages being flanked by isopropyl groups. Furthermore, the presence of a large number of isopropyl groups imparts hydrophobicity to Py-azo-COP, as confirmed by the increased adsorption of toluene compared to that of water in the pores of the COP.

favorable material to overcome the challenges of both selectivity and high capacity is still on. The introduction of CO₂-philic functional groups such as aminals, amines, triazines, and benzimidazole in the COP framework is an alternative way to enhance CO₂/N₂ selectivity and loading capacity.
Picric acid (PA) (or 2,4,6-trinitrophenol) is more explosive than trinitrotoluene, although it finds useful applications as a reagent in the dye, pharmaceutical, and leather industries. Further, it poses severe risks to human health as an allergen and is known to affect the central nervous system, cardiovascular system, kidneys, urinary system, and liver. It is also considered to be a potential carcinogen. In addition, PA, being water soluble, easily pollutes ground water and soil. Although most porous polymers (such as COPs) possess significant π-conjugation and structural similarities with π-conjugated fluorescent organic polymers, research on COPs has primarily focused on tuning the porosity and high gas uptake, whereas studies on the photophysical properties associated with sensing of PNACs are still in the early stages. While most MOFs or COFs employed for the chemosensing of PNACs lack hydrothermal stability, COPs usually possess better hydrothermal constancy.

Pyrene, a polycyclic π-conjugated molecule, being an excellent fluorophore with long fluorescence lifetimes and a high quantum yield, may serve as a good starting point to develop COPs for the simultaneous applications of CO$_2$ capture and nitroaromatics detection. In this context, we developed a new azo-linked porous COP based on a pyrene platform appended with sterically encumbered aniline and...
investigated its suitability as a chemosensor and CO₂ adsorption material. The details of this study are presented herein.

RESULTS AND DISCUSSION

Synthesis and Characterization. A pyrene substituted with four 2,6-diisopropylaniline rings, 1,3,6,8-tetrakis(4′-amino-3′,5′-diisopropylphenyl)pyrene (TADIPPy) (Scheme 1), was chosen as the monomer for the preparation of the azo-linked COP in the present study. The bulky isopropyl substituents were placed on the aniline part of the pyrene monomer for two reasons: (i) to increase the stability of the resultant COP toward water, acids, and bases through the expanded hydrophobic surface, and (ii) to enhance nitroaromatics detection and CO₂ adsorption by taking advantage of the ability of these bulky substituents to make the surface of the pores electron rich. This also ensured high CO₂/N₂ selectivity through enhanced Lewis acid−base interactions with −N=N− linkages.³f,¹⁸

The synthesis of the tetradiisopropylaniline-appended derivative of pyrene, TADIPPy, was accomplished starting from (4-((diphenylmethylene)amino)-3,5-diisopropyl-phenyl)boronic acid¹⁹ and 1,3,6,8-tetrabromopyrene.²⁰ The monomer 1,3,6,8-tetrakis(4′-amino-3′,5′-diisopropylphenyl)pyrene (TADIPPy) (2), was synthesized by Suzuki−Miyaura cross coupling of amine-protected boronic acid with 1,3,6,8-tetrabromopyrene followed by deprotection of the ketamine (1) through hydrolysis using dilute hydrochloric acid in tetrahydrofuran (THF) and subsequent neutralization with aqueous sodium hydroxide solution (Scheme 1). The polymer Py-azo-COP (3) was synthesized by the CuBr catalyzed homocoupling reaction of 2 using a catalytic amount of pyridine in a THF/toluene solvent mixture (v/v = 1:1) using air as the oxidant (Scheme 2).²¹ The reddish-brown precipitate obtained after the reaction was washed thoroughly with water and THF, soaked in concentrated HCl for 24 h, and then washed with 2 N aqueous NaOH. The product was then washed with copious amounts of water and ethanol. The sample was activated through solvent exchange with CHCl₃ and dried under vacuum for 12 h at 120 °C. TADIPPy and Py-azo-COP were exhaustively characterized by spectroscopic and analytical methods.

The optical characteristics of the building units, 1 and 2, were established from absorption spectroscopy. The absorption spectra of 1 and 2 show a red shift of approximately 70−80 nm from that of the simple pyrene (Figures S11 and S13). This large bathochromic shift can arise due to multiple reasons. First, the introduction of steric 2,6-diisopropylaniline groups at the 1, 3, 6, and 8 positions of the pyrene molecule is expected to lower the molecular planarity and symmetry. Secondly, the lone pair of electrons on the nitrogen atom of the amine groups conjugates with the aromatic system by donating its electron density to the aryl rings. This kind of bathochromic shift has been observed in many amine derivatives.²² Whereas 1 does not exhibit any observable fluorescence (Figure S12), 2 exhibits a strong blue fluorescence (Figure S15) with a high quantum yield (0.92, standard = quinine sulfate in 0.1 M H₂SO₄) and a lifetime of 2.8 ns in THF solution (Figure S17). Although the absorption spectra of 1 and 2 as a neat film exhibit a small red shift (Figures S14 and S16), the emission spectrum of 2 as a neat film show a bathochromic shift of 17 nm compared to that in the solution phase, which can be understood due to the

Figure 1. ¹³C CP-MAS NMR spectra of 3 (black) with 2 (gray) in the background.
aggregation behavior in the solid state (Figure S16). Solid state CP-MAS $^{13}$C NMR spectroscopy of Py-azo-COP showed signals from the $-\text{C}=-\text{N}=-\text{N}=-\text{C}=\cdot$ linkage at $\sim 147$ ppm in the CP-MAS $^{13}$C NMR spectrum (Figures 1 and S7), along with signals that correspond to other carbon atoms in the repeating unit of the polymer. In the Fourier transform infrared (FT-IR) spectrum of 3, bands were observed at 1166 and 1444 cm$^{-1}$, which can be attributed to the symmetric and asymmetric vibrations of the $-\text{N}=\text{N}=-\cdot$ bond (Figure S1). The thermogravimetric analysis (TGA) of the activated Py-azo-COP shows a marginal weight loss on heating under a dry nitrogen stream that is most likely due to the presence of adsorbed gases, moisture, or low molecular weight residual impurities (Figure S8). This is followed by slow decomposition on further heating. The amorphous nature of Py-azo-COP was confirmed by powder X-ray diffraction (XRD) analysis (Figure S9) and further by scanning electron microscopy (SEM) (Figure S10).

**Detection of PA.** The fluorescent pyrene moieties in this azo-linked polymer, Py-azo-COP, provide a suitable platform for the active detection of various kinds of electron-deficient nitroaromatic explosives by a fluorescent quenching response. Application of this kind of fluorescent porous architecture for the detection of nitroaromatic explosives is on the rise. The fluorescence spectrum of Py-azo-COP uniformly dispersed in THF exhibits a red shift (relative to the monomer 2) with broad greenish emission at around 485 nm, which tails up to 650 nm due extended $\pi$-conjugation in the polymer (Figure S19). The fluorescence quenching abilities of various analytes were investigated by dispersing Py-azo-COP in THF followed by sonication for 10 min.

Five different electron-deficient nitroaromatic compounds (PA, dinitrotoluene (DNT), p-dinitrobenzene (p-DNB), m-dinitrobenzene (m-DNB), and nitrobenzene (NB)) were employed in the fluorescence quenching studies. In addition to these nitroaromatics, the dispersion of Py-azo-COP was also titrated with electron-deficient molecules such as nitromethane (NM), hexafluorobenzene (HFB), and pentafluorophenol (PFP) to evaluate the selectivity. In all of the titrations, the fluorophore was excited at 415 nm. The fluorescence of Py-azo-COP was quenched by the successive addition of nitroaromatic compounds with different concentrations. Interestingly, the fluorescence was quenched more significantly (60% after the addition of 0.96 mM) by PA, compared to that of the other nitroaromatic compounds (Figure 2). The fluorescence intensity of Py-azo-COP diminished marginally after the addition of m-DNB and DNT whereas a slight decrease in intensity was observed after the addition of p-DNB. This selective detection of PA is highly promising for any practical application.

The quenching efficiency of Py-azo-COP toward various analytes was measured by employing the Stern–Volmer model (Figure 2b). The obtained Stern–Volmer constant $k_{SV}$ was found to follow the order PA >> p-DNB ~ DNT ~ m-DNB ~ NB >> NM, HFB, PFP for Py-azo-COP (Figure 2b and Table S3), and was moderate compared to those of the fluorophores reported for PA sensing (Table S6). The linear Stern–Volmer correlation observed suggests a static quenching mechanism is operating. To further confirm this, a time-correlated single-photon counting (TCSPC) experiment was conducted at the emission wavelength of 485 nm and excitation wavelength of 440 nm in THF. Py-azo-COP exhibits a biexponential decay.
with an average lifetime of 1.7 ns. After the addition of PA to Py-azo-COP, the lifetime remains almost unaffected \((\tau_0/\tau = 1)\), which indicates static quenching via ground state dark complex formation (Figures 3a and S21 and Table S4).\(^{17b,23a}\) Further, to ascertain the effectiveness of PA in quenching the fluorescence of Py-azo-COP in the presence of other PNACs, an additional set of experiments were performed. PA was added at regular intervals while titrating Py-azo-COP with other PNACs. As can be seen in Figure 3b, when PA is added during successive addition of other PNACs, there is a sharp decrease in fluorescence intensity, signifying the selectivity of Py-azo-COP toward PA.

**Gas/Solvent Adsorption Measurements.** The porosity of Py-azo-COP was investigated by nitrogen adsorption–desorption measurements. The \(N_2\) isotherm of Py-azo-COP at 77 K (Figure 4) exhibits a typical type I isotherm with rapid \(N_2\) uptake at very low partial pressures (0.0–0.1 bar) indicating predominant microporosity. Further, a slender hysteresis observed in the low pressure region suggests the presence of some mesopores in the Py-azo-COP framework. The Brunauer–Emmett–Teller surface area of Py-azo-COP was estimated to be 700 m\(^2\) g\(^{-1}\), which is comparable to other known azo-linked polymers (Table S5).\(^{3,18,21,24}\) To evaluate the pore size distribution (PSD), a nonlocal density functional theory method was used to fit the adsorption branch of the nitrogen isotherm. The PSD study shows that Py-azo-COP has three major peaks at 11.6, 14.8, and 19.7 Å (Figure 4, inset). This is due to the rampant formation of pores during polymerization. The pore volume of Py-azo-COP was calculated from the nitrogen gas adsorbed at \(P/P_0 = 0.99\) to be 0.41 cc g\(^{-1}\). The above results suggest that the pores in Py-azo-COP would be accessible for hosting various guest molecules such as \(CO_2\), \(H_2\), etc.

Because of its high thermal stability, micro/mesoporosity, and the presence of ample number of \(-N\equivN-\) phlic azo linkages, Py-azo-COP was investigated for selective \(CO_2\) adsorption. The \(CO_2\) isotherms measured at 273 and 298 K up to 1 bar were found to be completely reversible, exhibiting an uptake capacity of 8.5 wt % at 273 K (Figure 5a). This value of \(CO_2\) uptake is moderate as compared to those of previously reported azo-linked polymers (see Table S5). The azo-linked polymers constructed with flat aromatic platforms show higher selectivity toward \(CO_2\) due to the presence of \(-N\equivN-\) moieties and \(\pi\)-clouds in the polymer framework, thereby imparting \(N_2\)-phobic character to the material. However, in the present scenario, the presence of a large number of isopropyl groups that flank the \(-N\equivN-\) functionalities considerably reduce the affinity of the polymer toward \(CO_2\).

At zero coverage, the isosteric heat of adsorption (\(Q_{st}\)) calculated from the Classius–Clapeyron equation is 25.8 kJ mol\(^{-1}\), derived from the adsorption data collected at 273 and 298 K (Figure 5c), which is comparable to those of previously reported azo-linked porous polymers (Table S5). The unsaturation of \(CO_2\) uptake capacity at 1 bar prompted us to measure the \(CO_2\) uptake at higher pressure. The high pressure adsorption measurements show that \(CO_2\) adsorption saturates at 18.2 wt % at 273 K and 15.5 bar and at 16.6 wt % at 298 K and 22.0 bar (Figures S26–S27). Although the \(-N\equivN-\) functionalities in the polymer are flanked by isopropyl groups, Py-azo-COP shows higher selectivity toward \(CO_2\) as compared to that toward \(N_2\) and \(H_2\) at 273 and 298 K (Figures 5b and S25). The \(H_2\) sorption isotherms are completely reversible, indicating that the interaction between \(H_2\) and Py-azo-COP is weak. The observed uptake of \(H_2\) at 77 K and 1 bar is 1.02 wt % (Figure S24).
Ideal adsorbed solution theory (IAST) was used to analyze selectivity in binary mixture compositions of CO$_2$/N$_2$ (15:85) and CO$_2$/H$_2$ (20:80) utilizing the experimental single-component isotherms collected at 273 and 298 K. From a single-site Langmuir equation, the selectivity of the CO$_2$/N$_2$ (15:85) binary gas mixture at 273 and 298 K (1 bar) was...
calculated to be 11.9 and 28.6, respectively (Figure 6). These values are moderate compared to those of other reported azo-COPs (Table S5), and can be understood from the presence of isopropyl groups in the vicinity of the azo linkages. The selectivity of the CO\textsubscript{2}/H\textsubscript{2} (20:80) binary gas mixture at 273 and 298 K (1 bar) was found to be 45.0 and 63.1, respectively. CO\textsubscript{2}/N\textsubscript{2} selectivity was also calculated from the pure component isotherms of N\textsubscript{2} and CO\textsubscript{2} by an initial slope calculation method (Henry’s law) (Figures S28 and S29). It was found that CO\textsubscript{2}/N\textsubscript{2} selectivity was 41.5 and 37.3 at 273 and 298 K, respectively.

To investigate the low uptake of CO\textsubscript{2} by Py-azo-COP due to the presence of a large number of isopropyl groups, water and toluene vapor adsorption measurements were performed (Figure 5d). The interaction between polar water molecules and Py-azo-COP is weak, which can be seen from the shape of the water isotherm (type III) accommodating 3.5 wt % of water vapor (Figure 5d).\textsuperscript{26} In contrast, the toluene uptake capacity of Py-azo-COP is 20.8 wt % (6 times that of water uptake), which indicates its hydrophobic nature. The toluene isotherm has a typical type I profile, and the uptake saturates at P/P\textsubscript{0} ∼ 0.24, which indicates very strong interaction with the material. The presence of the alkyl group and π-cloud in the framework is most likely the primary reason for the high uptake capacity for toluene compared to that of water. CO\textsubscript{2}/H\textsubscript{2}O selectivity for the Py-azo-COP was found to be 3.1 (Figure S30).

### CONCLUSIONS

We designed and synthesized Cu(I)-mediated pyrene-based fluorescent Py-azo-COP, which exhibits (a) significant porosity with a high surface area of 700 m\textsuperscript{2} g\textsuperscript{-1}, (b) stability, and (c) high pore volume. The inherent fluorescent nature of Py-azo-COP led to the efficient and selective sensing of PA among other polynitroaromatic compounds such as DNT, p-DNB, and m-DNB, and other electron-deficient molecules. Because of the azo group’s CO\textsubscript{2}-philic nature, Py-azo-COP exhibits a CO\textsubscript{2} adsorption uptake of about 8.5 wt % of CO\textsubscript{2} at 273 K (up to 1 bar), which increases significantly to 18.2 wt % at 15.5 bar at the same temperature. However, the presence of isopropyl groups around the electron-rich azo linkages is detrimental to CO\textsubscript{2}/N\textsubscript{2} selectivity. The present results suggest that it would be interesting to investigate the gas sorption properties and sensing capabilities of structurally similar COPs, specifically by removing the bulky isopropyl substituents for further increased porosity and possibly higher sensing capabilities. Work in this direction is currently underway.

### EXPERIMENTAL SECTION

**Materials, Methods, and Instruments.** All of the reactions were carried out either under an aerobic or inert atmosphere as described. Solvents were purified according to standard procedures prior to use.\textsuperscript{27} Starting materials were purchased as bromine (Spectrochem Pvt. Ltd., India), tetraethyl orthosilicate (Sigma-Aldrich), benzophenone (Alfa Aesar), Pd(PPh\textsubscript{3})\textsubscript{4} (Sigma-Aldrich), 2,6-diisopropylaniline (Sigma-Aldrich), triisopropylborate (Alfa Aesar), n-BuLi (Acros), CuBr (Alfa Aesar), pyridine (Merck), and sodium carbonate (Merck) were procured from commercial sources and used without further purification. 1,3,6,8-Tetraphenyl-4-mesitylene and 4-((diphenylmethylene)amino)-3,5-diisopropylphenyl)boronic acid were synthesized and were prepared according to a known literature procedure.\textsuperscript{19,20} 2,4-Dinitrotoluene (Sigma-Aldrich), PA (Loba Chemie Pvt. Ltd., India), m-DNB (Thomas Baker (Chemicals) Pvt. Ltd., India), and p-DNB (Spectrochem Pvt. Ltd., India) were procured from commercial sources and used after crystallization from suitable solvents.

**Caution:** PA, DNB, and DNT are sensitive to external stimuli such as shock, heat, electromagnetic radiation, static electricity, etc. Although we did not face any kind of problems while working with them, it is highly advisable to handle these materials with due care.

The melting points were measured in open glass capillaries and are reported uncorrected. Infrared spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer as disks diluted in KBr. Microanalyses were performed on a Thermo Finnigan (FlashEA 1112) microanalyzer. NMR studies were performed on Bruker Avance DPX 400 and 500 MHz spectrometers.\textsuperscript{13}C CP-MAS NMR measurements were carried out on Bruker Avance 500 MHz spectrometers at 300 K and the samples were packed in 4.0 mm zircon rotor. The electrospray ionization-mass spectrometry (ESI-MS) studies were carried out on a Bruker MaXis impact mass spectrometer. TGA was carried out on a PerkinElmer Pyris thermal analysis system under a stream of nitrogen gas at the heating rate of 10 °C/min. Powder XRDs were recorded on a Philips X’pert Pro (PA) analytical diffractometer using Cu Kα radiation (λ = 1.54190 Å). The absorption spectra were recorded with a Varian Cary Bio 100 UV–vis spectrophotometer. The fluorescence spectral studies were performed on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a xenon flash lamp light source and a 1 cm path length quartz cuvette. Time-resolved fluorescence measurements were performed on a TCSPC system from IBH, U.K., employing a NanoLED-440 nm light source.

**Adsorption Measurements.** Adsorption measurements were performed on a Quantachrome Autosorb-1C analyzer using ultrahigh purity-grade N\textsubscript{2}, H\textsubscript{2} and CO\textsubscript{2} gases without further purification. N\textsubscript{2} and H\textsubscript{2} adsorption measurements were performed at 77 K in a liquid nitrogen bath. Adsorption measurements at 273 and 298 K for CO\textsubscript{2}, N\textsubscript{2}, and H\textsubscript{2} were performed in a water bath. Prior to gas adsorption measurements, the samples were evacuated at 120 °C for 5 h under ultrahigh vacuum (10\textsuperscript{-8} mbar) in an Autosorb-1C after transferring the compounds to the sample holder.

**Field Emission Gun Scanning Electron Microscopy (FEG-SEM).** The morphology of Py-azo-COP was studied using FEG-SEM on a JSM-7600F FEG-SEM operating at an accelerating voltage of 0.1–30 kV. The sample was prepared by drop casting the powdered sample onto a carbon substrate. The samples were sputtered with platinum prior to imaging.

**Photophysical Studies.** The UV–vis and fluorescence spectra of the building blocks (monomers) and Py-azo-COP were recorded at room temperature in THF solution and in suspension, respectively. One milligram of powdered Py-azo-COP was suspended in THF (5 mL) and sonicated for 10 min to obtain a homogeneous dispersion. The fluorescence spectra of the suspensions were measured by successive addition of polynitroaromatic analytes, keeping an excitation and emission slit width of 10 and 10 nm, respectively. Py-azo-COP was excited at 415 nm. The emission intensity (I) was plotted against wavelength to obtain quenching profiles. The values of the Stern–Volmer constant (K\textsubscript{SV}) were calculated by fitting the fluorescence data to the following equation.

\[
I/I_0 = 1 + K_{SV} [Q]
\]
where \( I_0 \) is the fluorescence intensity in the absence of the analyte, \( I \) is the fluorescence intensity in the presence of the analyte, and \( K_{SV} \) is the Stern–Volmer constant. The Stern–Volmer curves were obtained by plotting \( (I_0/I) \) versus analyte concentration. The slope of the curves yielded \( K_{SV} \).

The time-resolved fluorescence decays were collected with the emission polarizer at a magic angle of 54.7° and analyzed by IBH DAS v6.2 software. The full width at half-maximum of the instrument response function was 679 ps and the resolution was 56 ps per channel. The data were fitted to a monoexponential function using IBH DAS v6.2 data analysis software to obtain the excited state lifetime of Py-azo-COP with PA.

**Synthesis of 1.** (4-((Diphenylmethylene)amino)-3,5-diisopropylphenyl)boronic acid (1.694 g, 4.4 mmol), Na2CO3 (1.27 g, 12 mmol), and Pd(PPh3)4 (0.069 g, 0.06 mmol) were added to a mixture of THF/toluene (v/v = 1:1, 30 mL), 7.48 mmol (33 mL), and washed several times with water and cold hexane. The yellow product was then dried under vacuum.

The solution was cooled to room temperature and the yellow solid that precipitated out was filtered off and washed several times with water and cold hexane. The yellow product was then dried under vacuum. Yield: 0.615 g (39.5%), mp > 250 °C.1H NMR (CDCl3, 400 MHz): δ 8.06 (s, 2H), 7.97 (s, 4H), 7.89 (d, \( J = 6.9 \) Hz, 16H), 7.48–7.53 (m, 2H), 7.32 (s, 8H), 3.02 (sep, \( J = 2.8 \) Hz, 8H), 1.26 (d, \( J = 6.4 \) Hz, 12H), 1.0 (d, \( J = 6.64 \) Hz, 12H) ppm.13C NMR (CDCl3, 100.61 MHz): δ 163.4, 146.0, 137.9, 136.1, 135.9, 130.6, 129.5, 129.2, 128.4, 128.1, 127.8, 125.6, 125.0, 28.6, 24.2, 22.2. FT-IR (KBr, cm\(^{-1}\)): 3420 (br), 3056 (m), 2959 (s), 2867 (m), 1639 (br), 1620 (s), 1532 (m), 1350 (w), 1302 (w), 1237 (w), 1178 (m), 953 (m), 696 (vs). Anal. Calcd for C116H120N4: C, 83.90; H, 7.11; N, 3.59. Found: C, 83.91; H, 7.24; N, 3.82.

**Synthesis of TADIPPpy (2).** Compound 1 (1.560 g, 1.0 mmol) was dissolved in THF (20 mL) and HCl (2 N, 20 mL) was added. After the solution was stirred at 60 °C for 12 h, the solvent was removed by rotary evaporation. The white solid was thoroughly washed with diethyl ether and cold THF to remove the generated benzophenone and the hydrochloride salt was dried under vacuum. To a suspension of the salt in THF (25 mL), an aqueous NaOH solution (1.0 N, 50 mL) was added and stirred for 6 h at room temperature. The mixture was then extracted with diethyl ether. The ether extracts were collected and the product was further extracted from the water phase with additional diethyl ether (30 mL). The organic phase was combined and dried with anhydrous MgSO4. The solvent was removed using a rotary evaporator to give a yellow solid as the free amine. Yield: 0.52 g (90%), mp > 250 °C.1H NMR (CDCl3, 400 MHz): δ 8.22 (s, 2H), 8.06 (s, 4H), 7.40 (s, 8H), 3.87 (s, 8H), 3.05 (sep, 8H), 1.35 (d, \( J = 6.6 \) Hz, 48H) ppm.13C NMR (CDCl3, 100.61 MHz): δ 139.7, 137.9, 132.6, 131.6, 129.5, 127.9, 126.8, 125.8, 125.2, 28.4, 22.7. FT-IR (KBr, cm\(^{-1}\)): 3478 (m), 3406 (m), 2959 (s), 2867 (m), 1620 (s), 1462 (s), 1443 (s), 1350 (w), 1317 (w), 1064 (w), 883 (w). Anal. Calcd for C36H29N4: C, 85.09; H, 8.70; N, 6.20. Found: C, 84.96; H, 8.58; N, 6.58. ESI-MS: \([M + K]^+\) m/z ~ 941.599.

**Synthesis of Py-azo-COP (3).** To a mixture of 2 (280 mg, 0.30 mmol) in a mixture of THF/toluene (v/v = 1:1, 30 mL), CuBr (21.5 mg, 0.150 mmol) and pyridine (83 mg, 1.05 mmol) were added. The reaction mixture was stirred under ambient aerobic conditions for 24 h followed by heating at 80 °C for 2 days. The dark red reaction mixture was filtered and washed with excess THF and water. The dark red powder thus obtained was treated with aqueous HCl (100 mL, 4 M) for 24 h and then filtered and washed with distilled water. The dried powder was then further washed with aqueous NaOH (200 mL, 1 M) followed by further washing with distilled water and ethanol. Yield: 205 mg (74%), mp > 250 °C. FT-IR (KBr, cm\(^{-1}\)): 3404 (br), 2959 (vs), 2926 (s), 2871 (s), 1622 (s), 1600 (s), 1461 (vs), 1444 (s), 1384 (m), 1299 (w), 1250 (w), 1217 (w), 1166 (m), 1101 (m), 1068 (w), 882 (m). Anal. Calcd for C64H70N4: C, 85.86; H, 7.88; N, 6.26. Found: C, 78.86; H, 7.02; N, 5.23. The difference between the observed and theoretical elemental analysis values is common among porous organic polymers and is caused by incomplete polymerization as well as the adsorption of water and gas molecules. This was further confirmed by the initial weight loss of about 15% below 100 °C in the TGA.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00515.

FT-IR; NMR; absorption and fluorescence spectroscopic data for monomer and polymer; fluorescence spectra and fluorescence quenching profiles of CO2, H2, and N2 sorption profiles of the Py-azo-COP (PDF)

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Notes

The authors declare no competing financial interest.

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