

Supporting Information

Rigid *versus* Flexible Ligands on Carbon Nanotubes for the Enhanced Sensitivity of Cobalt Ions

*Pingping Gou, Nadine D. Kraut, Ian Matthew Feigel, and Alexander Star**

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA

National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA 15236, USA

[*] Department of Chemistry

University of Pittsburgh

Pittsburgh, PA 15260

Tel: (412) 624-6493

Fax: (412) 624-6008

Email: astar@pitt.edu

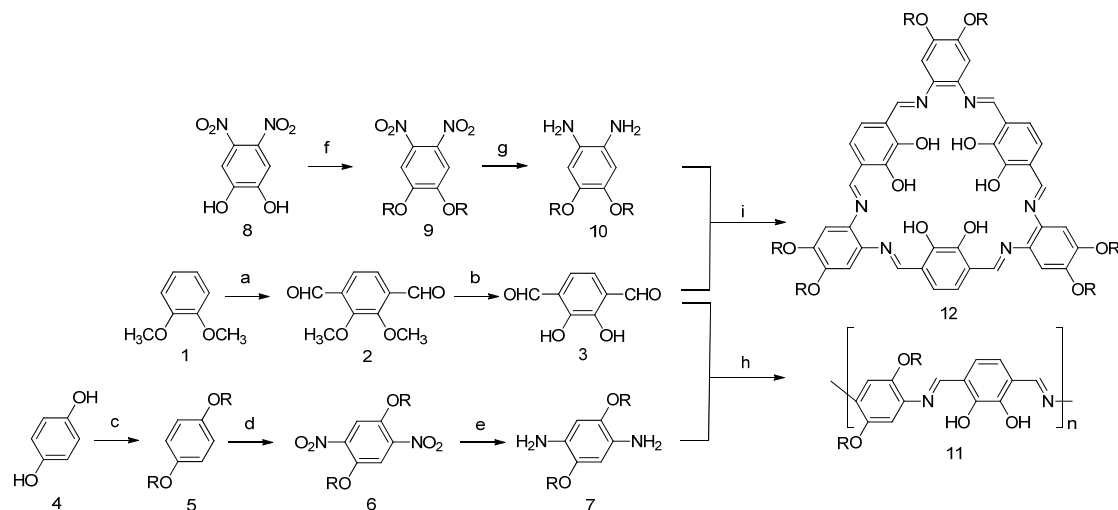
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Experimental Section:

Materials and Instrumentation. Chemicals were purchased from Aldrich and used as received. Solvents were dried, distilled, and stored under argon. All reactions were carried out under N₂ atmosphere unless otherwise stated. Column chromatography was performed using Merck silica gel 60. Melting points (mp) were determined on an Electrothermal melting apparatus and are uncorrected. UV/Visible spectra were obtained using a PerkinElmer Lambda 900 spectrophotometer. FT-IR spectra were recorded as thin film on NaCl plates or as KBr pellets on an Avatar 380 Nicolet FI-IR spectrometer. Proton and carbon nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Bruker DPX 300 (300 MHz) NMR spectrometer at 25°C, using the deuterated solvent as lock and the residual solvent as internal standard. Electron impact ionization mass spectrometry (EI-MS) was performed on a VG-AutoSpec instrument. High resolution mass spectra were taken on a VG-Autospec double focusing spectrometer. Molecular weights of polymers were determined by using a Waters Gel Permeation Chromatography system equipped with Waters 510 HPLC pump, phenogel columns and a Waters 410 Differential Refractometer at a flow rate of 0.4 mL/min. All molecular weights were measured against polystyrene standards in THF. Cyclic voltammograms (CV) were recorded using CH electroanalyzer instrument (CHI 604C, CH Instruments, Austin, TX) with a scan rate of 0.1 V/s at an interval of 0.001 V.

Scheme S1 Synthesis of polyazomethine (PAM) and salophen macrocycle (MAC)^a



^aReagents and Conditions: (a)(i) n-BuLi, TMEDA, Et₂O, reflux, 10 hr. (ii) DMF, H₂O, HCl, 28%; (b) BBr₃, CH₂Cl₂, then H₂O, 90%; (c) C₈H₁₇Cl, K₂CO₃/DMF, 80 °C, 36 h, 98%; (d) HNO₃/AcOH, 27%; (e)(i) 10% Pd/C, N₂H₄, EtOH, reflux, 70%; (ii) recryst, hexane, 46%; (f) C₈H₁₇Br, CS₂CO₃/DMF, 100 °C 3 h, 60%; (g) 10% Pd/C, N₂H₄, EtOH, reflux, 86%; (h)(i) LiCl/DMAP/HMPA/NMP, RT, 56%; (ii) CHCl₃/MeCN, 90 °C, 2 hr, 70%

1,2-Dimethoxy-3,6-diformylbenzene (2).^{S1} Tetramethylethylenediamine (TMED) (4.61 mL, 180 mmol) was added to a solution of 1,2-dimethoxybenzene (**1**) (4.61 mL, 36mmol) in 50 mL of anhydrous Et₂O at RT. A 1.6 M solution of n-BuLi in hexane (112.65mL, 180 mmol) was added dropwise to the reaction mixture at 0°C. The mixture was then heated under reflux for 10 hours to form a grey yellow organolithium salt intermediate. After cooling to 0°C, anhydrous dimethylformamide (DMF) (13.30 mL, 180 mmol) was added and the reaction mixture and stirred for an additional 30 min. To the resulting orange mixture, 100 mL of H₂O and 40 mL of 3M HCl were added and the product was extracted into 100 mL of Et₂O three times. The product was then washed with H₂O, dried in Na₂SO₄, and the solvent was evaporated off. The product mixture was separated by column chromatography (SiO₂: Hexane/EtOAc, 10:1), and crystallization from petrol ether yielded 1,2-dimethoxy-3,6-diformylbenzene as a light yellow solid (1.98 g, 28%). m.p. 72-88 °C (light petroleum). ¹H-NMR (CDCl₃) δ 10.43 (2H, s, CHO), 7.62 (2H, s, aromatic CH), 4.05 (6H, s, OMe).

3,6-Diformylcatechol (3).^{S2} A 1.0 M solution of BBr₃ in 8.51 mL (8.51 mmol) of CH₂Cl₂ was added dropwise through a septum with use of a syringe to a stirred solution of 500 mg (2.6 mmol) 1,2-dimethoxy-3,6-diformylbenzene (**2**) in 5mL of dry CH₂Cl₂ at -78 °C. The reaction mixture was stirred under inert atmosphere for an additional 40 min at room temperature. The reaction mixture was subsequently poured into 50 mL of ice water, stirred for 40 min, and then saturated with NaCl salt. The product was isolated by extraction into 30 mL of CH₂Cl₂ three times, washed with H₂O, dried in Na₂SO₄, and evaporated to afford 3,5-diformylcatechol as a grassy yellow solid (388 mg, 90%). m.p. 143-145°C (hexane). ¹H-NMR (DMSO-D₆) δ 10.28 (2H, s, CHO), 7.25 (2H, s, aromatic CH). EI, m/e (relative intensity): 166.03 (100). HR EI-MS: calcd. For C₈H₆O₄ (M⁺) 166.0266; found 166.0265. Anal. Calc'd for C₈H₆O₄ : C, 57.87; H, 3.64. Found: C, 58.08; H, 3.79.

1,4-Dioctyloxybenzene (5). A solution of hydroquinone (**4**) (11 g, 0.1mmol), of 1-chlorooctane (51 mL, 0.3 mol), and of K₂CO₃ (69 g, 0.5 mol) in 200 mL of DMF was heated for 36 h at 80°C. After

cooling, the precipitate was filtered off, and the solution was concentrated under high vacuum. The product was isolated by precipitation with MeOH to afford 1,4-dioctyloxybenzen as white solid (23g, 98%). Mp 55-56°C. ¹H-NMR (CDCl₃) δ 6.82 (4H, s, aromatic CH), 3.89 (4H, t, ³J_{HH} = 6.6 Hz, OCH₂), 1.75 (4H, m, CH₂), 1.44 (20H, m, CH₂), 0.88 (6H, t, ³J_{HH} = 6.0 Hz, CH₃).

1,4-Dioctyloxy-2,5-dinitrobenzene (6). Concentrated HNO₃ (25 mL) was added dropwise to a solution of 1,2-dioctyloxybenzene (**5**) (15.2 g, 45.5 mmol) in 50 mL of glacial AcOH. (Caution: extremely exothermic reaction). The reaction mixture was then heated at 80-90°C for additional 5 min and another 25 mL of concentrated HNO₃ was added. After cooling, 500 mL of iced water was added to the reaction mixture, and the yellow precipitate was filtered from the solution. The product is a mixture of *p*-dinitrobenzene and *o*-dinitrobenzene, and they were subsequently separated by column chromatography (SiO₂: Hexane/EtOAc, 30:1 then 10:1). Crystallization from EtOH yielded 1,4-dioctyloxy-2,5-dinitrobenzene as yellow sheet crystals (5.2 g, 27%): Mp 100-101°C. ¹H-NMR (CDCl₃) δ 7.52 (2H, s, aromatic CH), 4.10 (4H, t, ³J_{HH} = 6.4 Hz, OCH₂), 1.84 (4H, m, CH₂), 1.33 (20H, m, CH₂), 0.90 (6H, t, ³J_{HH} = 6.6 Hz, CH₃). Anal. Calc'd for C₂₂H₃₆N₂O₆: C, 62.24; H, 8.55; N, 6.60. Found: C, 62.22; H, 8.65; N, 6.53.

1,4-Dioctyloxy-2,5-phenylenediamine (7). To a solution of 1,4-dioctyloxy-2,5-dinitrobenzene (**6**) (580 mg, 1.37 mmol) in 40 mL of EtOH, 10% Pd/C (40 mg) and of hydrazine monohydrate (2.5 mL, 51 mmol) were added. The resulting solution was heated at 80°C for 5 h, and brownish red solution became colorless. After cooling to room temperature, the catalyst was filtered out and EtOH was evaporated under reduced pressure. 20 mL of hexane was added to the flask and kept in the freezer overnight to provide the pure product 1,4-dioctyloxy-2,5-diaminobezene as a white precipitate (220 mg, 46%). ¹H-NMR (CDCl₃) δ 6.34 (2H, s, aromatic CH), 3.90 (4H, t, ³J_{HH} = 5.47 Hz, OCH₂), 1.73 (4H, m, CH₂), 1.28 (20H, m, CH₂), 0.88 (6H, t, ³J_{HH} = 6.69 Hz, CH₃). EI, *m/e* (relative intensity): 364.31 (83). HR EI-MS: calcd. For C₂₂H₄₀N₂O₂ (M⁺) 364.3090; found 364.3096.

1,2-Octyloxy-4,5-dinitrobenzene (9).^{S3} To a mixture of 4,5-dinitrocatechol (**8**) (302 mg, 1.5 mmol) and Cs₂CO₃ (984 mg, 3.0 mmol) in DMF (5 mL), 1-bromooctane (0.78 mL, 4.5 mmol) was added. The resulting mixture was stirred for 3h at 100 °C under a N₂ atmosphere. After evaporation of the mixture, the product was purified by column chromatography (SiO₂, hexane/EtOAc = 40/1) to yield 1,2-octyloxy-4,5-phenylenediamine as a yellowish solid (382 mg, 60%)

1,2-Octyloxy-4,5-phenylenediamine (10). To a solution of 1,2-Octyloxy-4,5-dinitrobenzene (**9**) (580 mg, 1.37 mmol) in EtOH (40 mL), 10% Pd/C (40 mg) and hydrazine monohydrate (2.5 mL, 15 mmol) were added. After 5h of refluxing, the hot solution was filtered through Celite. After cooling, the white precipitate was filtered off and rinsed with chilled MeOH to yield 1,2-octyloxy-4,5-diaminobenzene (430 mg, 86%). The diamine is quite unstable to storage and the following steps were carried out immediately.

Polyazomethine (PAM) polymer (11). Freshly prepared 1,4-dioctyloxy-2,5-phenylenediamine (109 mg, 0.3 mmol) was added to a solution of 3,6-diformylcatechol (50 mg, 0.30 mmol), LiCl (55 mg, 1.2 mmol) and 4-dimethylaminopyridine (DMAP) (3.7 mg, 0.03 mmol) in a mixture of 3 mL of hexamethylphosphoramide (HMPA) and 3 mL of anhydrous methylpyrrolidone (NMP). The reaction mixture (deep orange red color) was stirred for 48 hours under ambient conditions. 23 μ L (0.15 mmol) of t-butyraniline was added to the solution and the resultant mixture was stirred for additional 6 hours. The resulting precipitate (polymer) was extracted from MeOH (200 mL), and washed thoroughly with MeOH and distilled water. PAM polymer was further purified by washing with MeOH in a Soxhlet extractor for 12 h to afford a brown orange solid (83 mg, 56%). $\nu_{\text{C=N}}$, 1614 cm⁻¹; $\nu_{\text{O-C-O}}$ 1215 cm⁻¹; ¹H-NMR (CDCl₃) δ 12.71 (2H, s, OH), 8.63 (2H, s, CH=N), 7.48 (4H, d, aromatic CH), 4.03 (4H, m, OCH₂), 1.89 (m, CH₂), 1.35 (m, CH₂), 0.88 (t, ³J_{HH} = 6.3 Hz, CH₃). The number average molecular weight (M_n = 24,600 g/mol) and polydispersity index (PDI = 1.4) of polymer were determined in THF

by Gel Permeation Chromatography (GPC) against polystyrene standards in THF. Anal. Calc'd for $(C_{30}H_{42}N_2O_4)_n$: C, 72.84; H, 8.56; N, 5.66. Found: C, 73.08; H, 8.60; N, 5.71.

Salophen Macrocycle (MAC) (12).^{S3} MAC was synthesized following published procedure.^{S3} 1,2-dioctyloxy-4,5-phenylenediamine (1.9 g, 6.0 mmol) was dissolved in 60 mL of 1:1 degassed $CHCl_3$:MeCN under a N_2 environment. 3,6-diformylcatechol (1.0 g, 6.0 mmol) was added, changing the appearance of the solution from colorless to deep red. After heating at 90 °C while refluxing for 2 h, the solution was cooled down to room temperature, yielding red needles of salophen macrocycle, which were isolated on a funnel, washed with chilled MeCN, and dried under vacuum. Yield: 92 mg, 71%. ; 1H -NMR ($CDCl_3$) δ 8.56 (6H, s, CH=N), 7.01 (6H, s, aromatic CH), 6.78 (6H, d, aromatic CH), 4.05 (12H, t, $^3J_{HH} = 5.6$ Hz, OCH_2), 1.88 (12H, m, CH_2), 1.52 (12H, m, CH_2), 1.32 (24H, m, CH_2), 0.91 (t, $^3J_{HH} = 6.0$ Hz, CH_3).

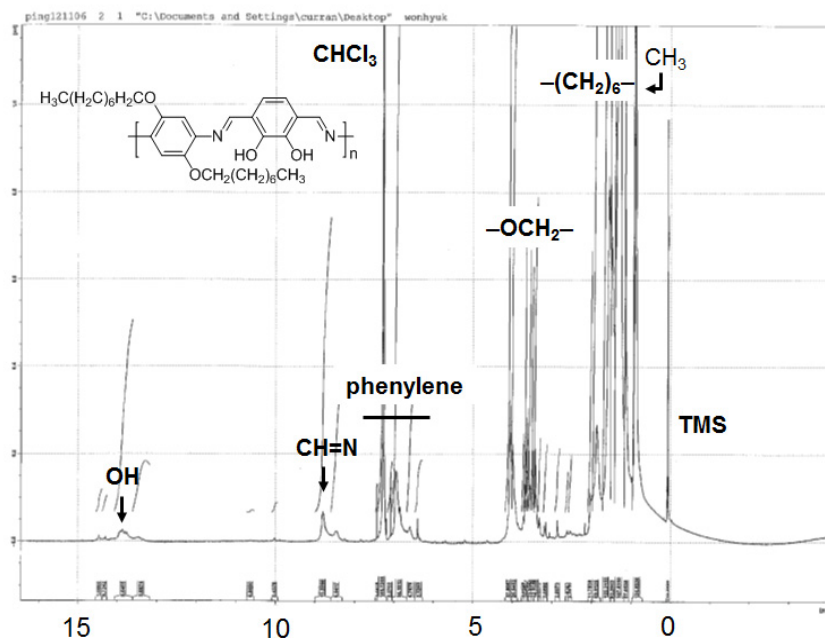


Figure S1. ^1H -NMR (CDCl_3 , 300 MHz) of PAM polymer.

The ^1H NMR spectrum is in good agreement with the polymeric structure. Additionally, the presence of a major signal at $\delta = 8.77$ ppm for the azomethine protons suggests the predominance of one isomer, which presumably is the thermodynamically more stable *anti* isomer. The broader signal at $\delta 12.7$ ppm corresponds to hydroxyl protons, the integration of O-H proton gives a number less than the expected number of protons on the hydroxyl groups, which is due to the fact that protons on heteroatoms such as oxygen can undergo rapid proton-deuterium exchange with water. The end groups of the polymer such as $-\text{NH}_2$ and $-\text{CHO}$ is barely seen on the spectrum, indicating a degree of polymerization higher than ten.

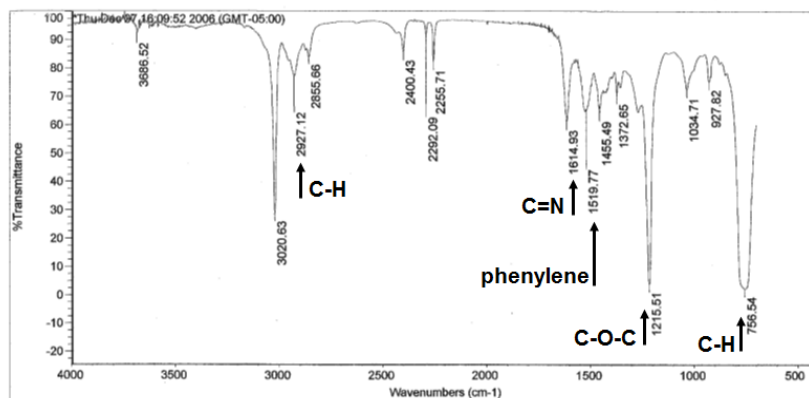


Figure S2. FTIR (NaCl) spectra of PAM polymer.

The FTIR spectrum shows a strong absorption band at 1614 cm^{-1} assigned to the imine ($\text{C}=\text{N}$) stretching. This band is shifted to a higher wavenumber compared to other PAM polymers, suggesting strong intramolecular hydrogen bonding between the imine nitrogen and phenol hydrogen ($\text{O}-\text{H}\cdots\text{N}=\text{C}$) in the *ortho*-position of the azomethine aromatic ring.

Additionally, elemental analysis was consistent with the chemical composition of the polymer, and Gel Permeation Chromatography (GPC) analysis indicated degree of polymerization of 68 ($M_n = 24,600\text{ g/mol}$ and $\text{PDI} = 1.4$).

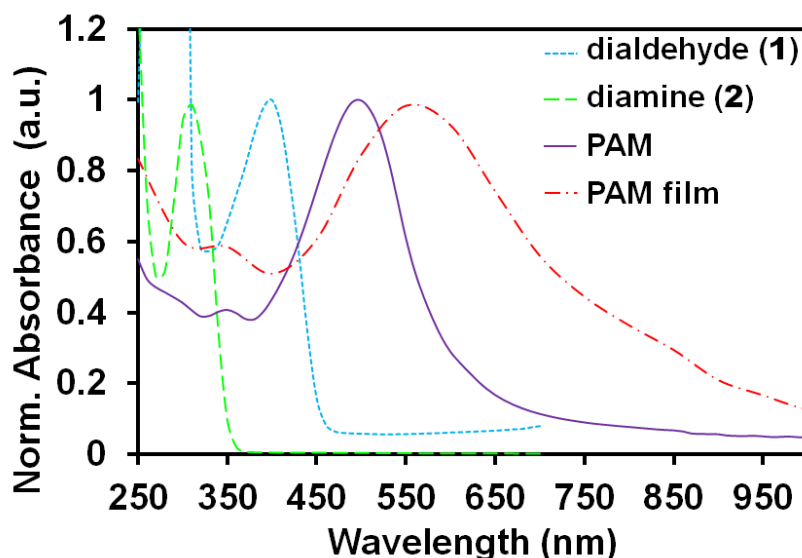


Figure S3. UV-vis-NIR absorption spectra of PAM in solution (THF) and as a solid film deposited onto a quartz plate.

Spectra of PAM's constituent monomers, 1,4-dioctyloxy-2,5-phenylenediamine (diamine (1)) and 3,6-diformylcatechol (dialdehyde (2)), in THF are also given for a comparison. PAM exhibits a main band centered at 492 nm and a weaker band around 346 nm which is associated with the π - π^* and n - π^* transitions in the polymer backbone, respectively. The main absorption band of PAM is significantly red shifted in comparison to both starting monomers; 1,4-dioctyloxy-2,5-phenylenediamine ($\lambda_{\text{max}} = 307$ nm) and 3,6-diformylcatechol ($\lambda_{\text{max}} = 394$ nm). This shift can be attributed to the increased degree of π conjugation in the polymer backbone compared to the reactants. When PAM is deposited as a thin film, the absorption band of PAM film was broadened and further red shifted (~ 80 nm). This shift can be expected for polymer films due to an increased planarity induced by interchain stacking in the solid state.^{S4}

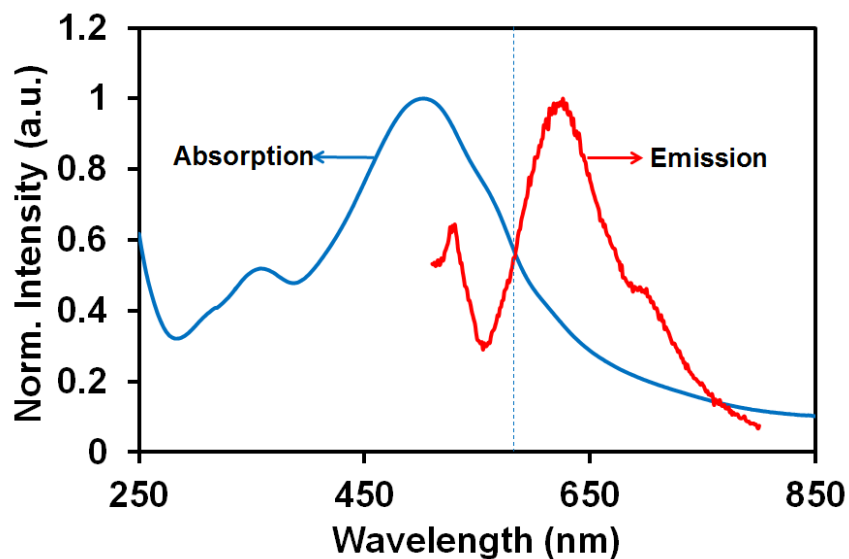


Figure S4. Normalized absorption and emission spectra of PAM polymer in THF.

Normalized absorption and emission spectra of PAM polymer in THF allow for estimation of the bandgap of the conducting polymer to be ca. 2.1 eV from the intercept of the normalized absorption and emission spectra. However, this energy gap is somewhat smaller than that of prototypical PAM polymer without phenol groups, reported previously to be 2.4 eV.^{S5} The difference in the band gap values suggests that intramolecular hydrogen bonding ($\text{OH}\cdots\text{N}$) stabilizes the backbone of the macromolecule by reducing the rotation freedom of the azomethine ring.

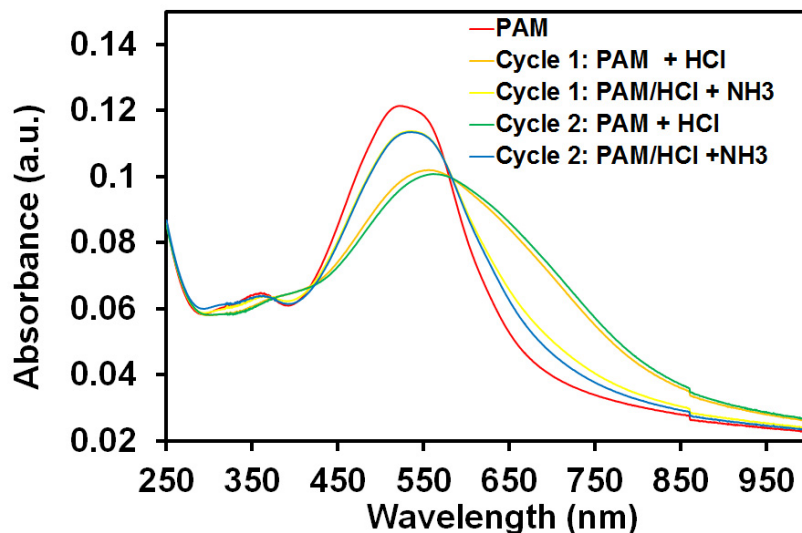


Figure S5. Absorption spectra of PAM polymer thin film on quartz plate and the response upon treatment with HCl and NH₃ vapors.

Treatment of the film with acidic vapors results in a color change of PAM film from deep red to light blue and a red shift (35 nm) of the main peak with decreased intensity. This change is most likely due to protonation of the imine nitrogen, which disrupts the $n-\pi$ conjugation between imine nitrogen lone pair electrons and the adjacent phenylene ring. Compared to metal ion complexation, protonation has similar color change but a much smaller red shift. Treatment with basic vapors, which will deprotonate the polymer backbone, changes the film color back to red, and a 20 nm blue shift is observed in the UV-Vis absorption spectrum. The absorption maximum does not return to the original position most likely due to the loss of intramolecular hydrogen bonding from the addition of NH₃ vapors. It is worth mentioning that the protonation and deprotonation of the PAM thin film after the second cycle are reversible and can be repeated without significant degradation.

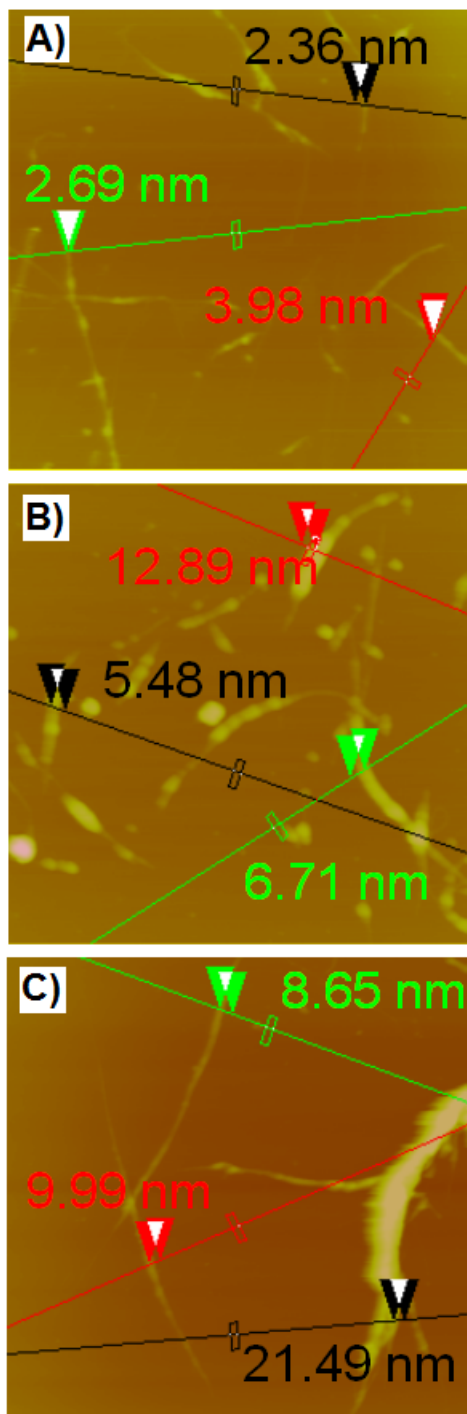


Figure S6. AFM images and section analysis of (A) bare SWNT, (B) MAC/SWNT, (C) and PAM/SWNT.

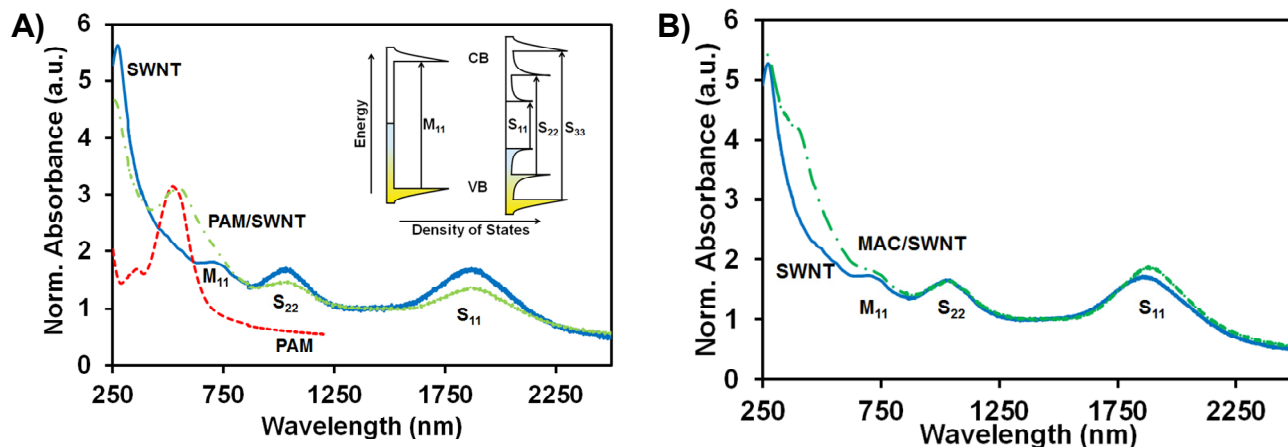


Figure S7. A) UV-vis-NIR absorption spectra of SWNT (blue), PAM (red) and PAM/SWNT (green). Inset: Density of states (DOS) diagram showing the electron transitions in SWNTs. B) UV-vis-NIR absorption spectra of SWNT (blue) and MAC/SWNT (green).

A peak at 392 nm appears upon addition of MAC to a SWNT suggesting that MAC is non-covalently attached to the SWNT film. The S_{11} band of SWNT film is shifted from 1847 to 1875 nm (a 28 nm red-shift) upon attachment, supporting the assumption of π - π stacking interactions. These interactions play an important role in electron transport of the SWNT device. The increased absorption intensity of the S_{11} transition can be attributed to electron transfer from the higher HOMO of MAC toward the lower valence band of SWNT. Another possible factor is the electron donor hydroxyl groups in the MAC modified SWNT complex. Although these interactions are individually weak, the involvement of π - π stacking interactions and electron-donor transfer along the MAC/SWNT complex provides a stable, non-covalently functionalized SWNT device.

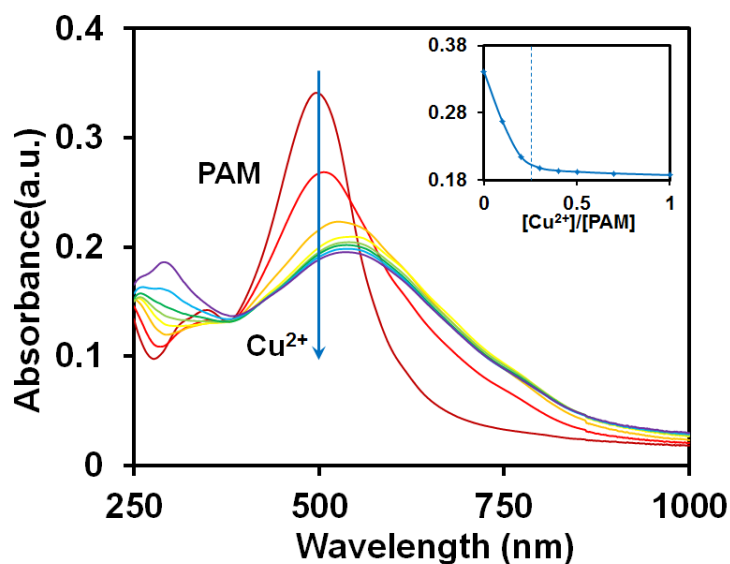


Figure S8. UV-Vis titration of PAM polymer with CuCl_2 . The inset shows the absorption intensity of the complex ($\lambda_{\text{max}}=500\text{nm}$) as a function of Cu^{2+} to PAM ratio, where the concentration of PAM is 10^{-4} M.

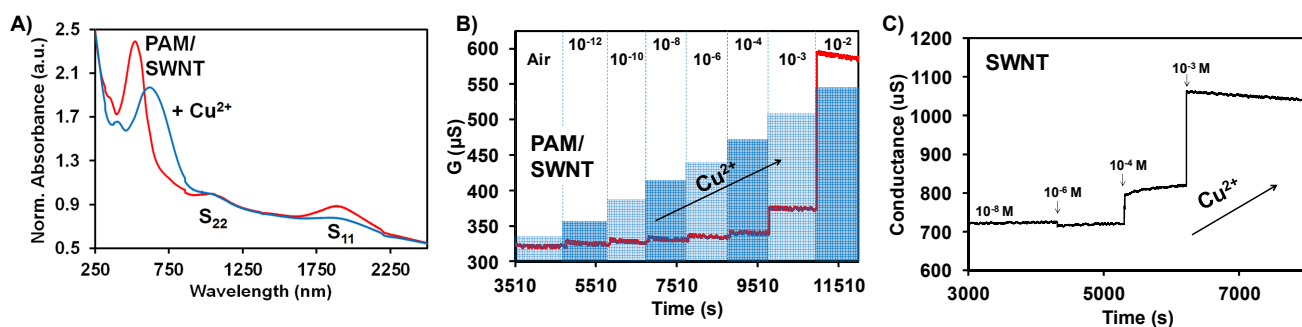


Figure S9. A) UV-Vis-NIR absorption spectra of a PAM/SWNT film (red) and the film upon addition of 10^{-2} M Cu^{2+} ions (blue). B) Conductance dependence of PAM/SWNT to varying concentrations (M) of Cu^{2+} ions. C) Real-time conductance measurements of bare SWNT for varying concentration of Cu^{2+} ions.

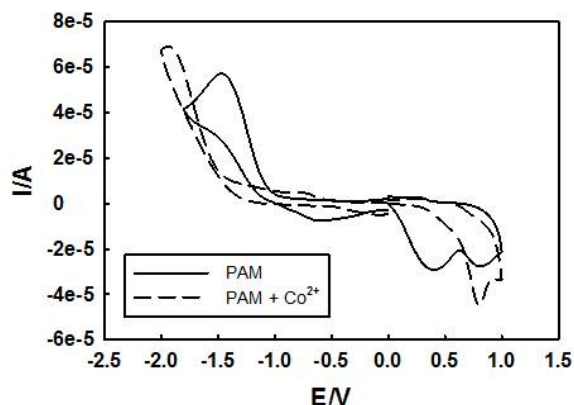


Figure S10: Cyclic voltammograms of PAM polymer (solid line) and PAM + Co^{2+} (dashed line). The significant change in the CV curves upon addition of Co^{2+} correlates with a change in the relative donating ability of the polymeric material.

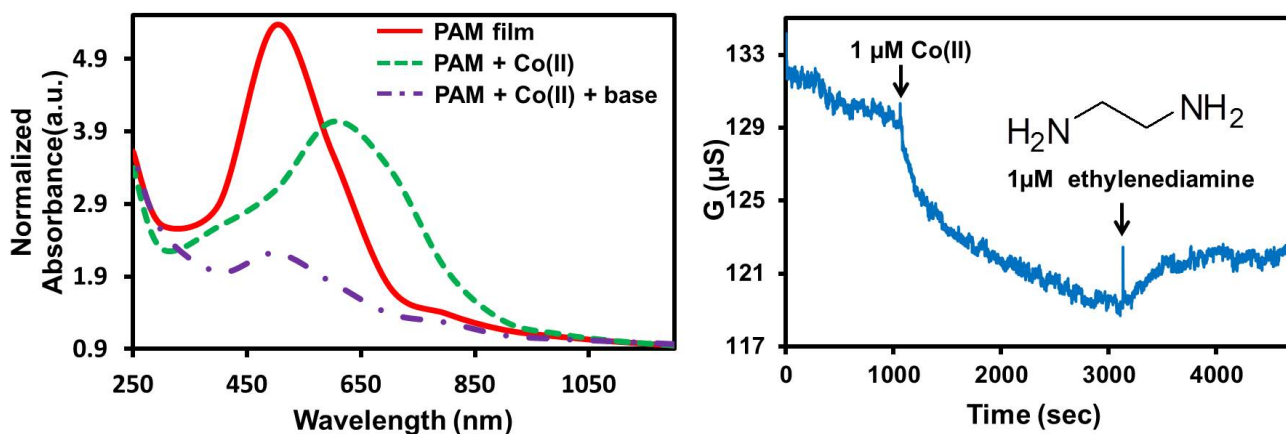


Figure S11: The addition of ethylenediamine shows a reversible response due to the competitive binding of Co^{2+} ions. The signal is not fully reversed and could be due to two different factors. One factor being that the SWNT film is somewhat dissolved in the MeCN solvent. Therefore, some of the film is washed off the device causing a lower absorbance and a drop in conductivity. A second factor is that the device being tested is a film. The analytes are administered in drop form and dried onto the SWNT network. Therefore, even though the first formation constant of the ethylenediamine + Co^{2+} complex was reported^{S6} to be $7.8 \times 10^5 \text{ M}^{-1}$ and the association constant of the PAM + Co^{2+} was calculated to be 2.5×10^5 , the ability of the ethylenediamine to thoroughly interact with all of the Co^{2+} is limited.

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