Electronic Supplementary Information for

Unusual Solvent-Dependent Photophysical and Self-Assembly Properties of NO_2 Substituted T-Shaped Phenazines

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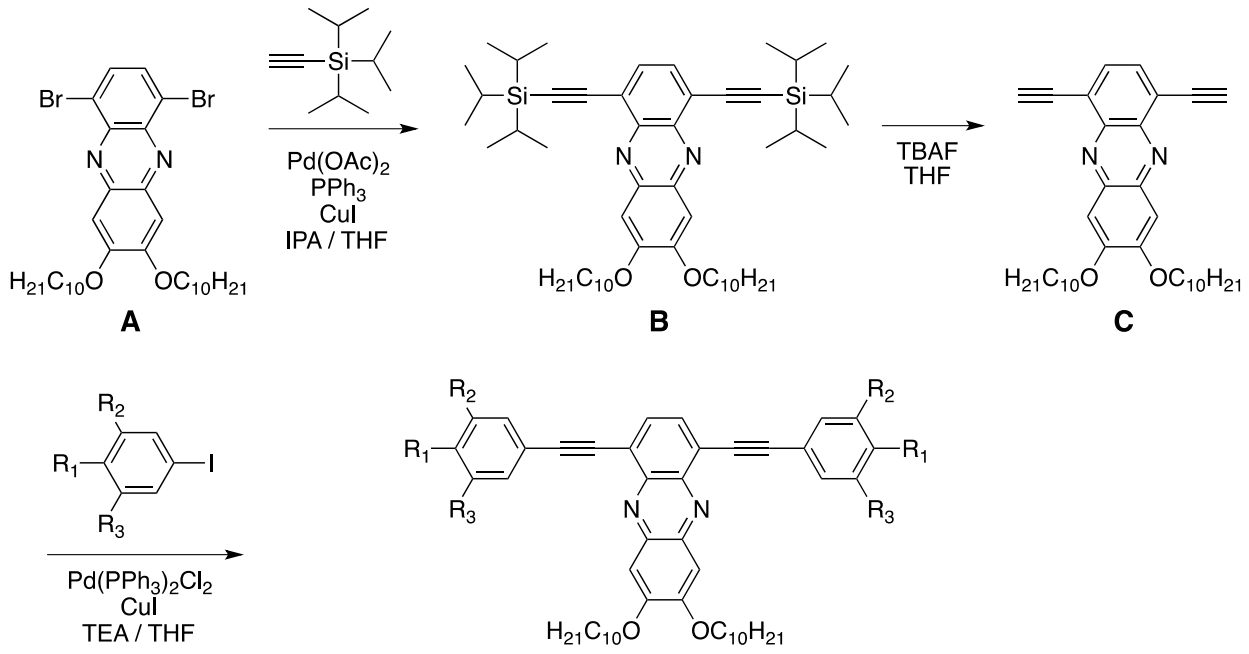
General Instrumentation: Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 400 MHz NMR spectrometer at room temperature. Deuterated chloroform ($CDCl_3$) containing tetramethylsilane (TMS) as internal standard was used as the solvent for both ^1H NMR and ^{13}C NMR. The mass spectra were recorded at the University of Illinois at Chicago. Optical properties of the molecules were obtained with Shimadzu UV-2450 UV-visible spectrophotometer and Horiba Fluorimeter using a xenon lamp for the excitation source for absorption and fluorescence emission, respectively. Electrochemistry measurements were performed with CV on a CH instrument 660C with a three electrode configuration, with a cell equipped with a platinum plate as the counter electrode, a platinum disc as the working electrode (2 mm diameter), and a non aqueous Ag/Ag^+ electrode (Ag in 10 mM $AgNO_3$ solution in acetonitrile) as the reference electrode. CV measurements for all compounds were recorded in methylene chloride solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. All solutions were purged with Ar for 15 - 20 min before each experiment, and a blanket of Ar gas was used during the experiments. The scan rate (ν) was adjusted to 100 mV/s for all experiments. All potentials were calibrated to the ferrocene/ferrocenium (Fc/Fc^+) redox couple. Fourier transform infrared spectroscopy (FT-IR) measurements were performed using an IRPrestige-21 Shimadzu spectrometer. A diluted solution of compounds in carbon tetrachloride (CCl_4) was measured in a potassium bromide (KBr) cell with 1 mm spacing at room temperature. The xerogel samples were prepared on a sodium chloride (NaCl) plate, followed by air drying. Thermal gravimetric analyses were performed under a nitrogen flow at a heating rate of 10°C/min using a TA instrument TGA-Q50. Differential Scanning Calorimetric (DSC) analyses were performed under a nitrogen flow at heating and cooling rates of 5°C/min using a TA instrument 2010 DSC. FE-SEM images were obtained using a JEOL field-emission SEM JSM-6700F with an operating voltage of 5.00kV. Samples were prepared on a gold/mica substrate followed by air drying, and were then coated with gold for 35 seconds. X-ray diffraction (XRD) patterns were collected on a Pananalytical X'Pert PRO X-ray diffractometer, for which a Cu-Kα radiation (λ = 1.54 Å, 20 mA, 40 kV) was used.

Synthesis and Characterization of Compounds: All chemicals and solvents were purchased from commercial source and used as received without further purification. 1,4-Dibromo-7,8-bis(decyloxy)phenazine (**A**)[1] and 1-iodo-3,4-dinitrobenzene[2] were synthesized according to the literature procedures.



T-pNT: $R_1 = NO_2$, $R_2 = R_3 = H$ **T-34dNT**: $R_1 = R_2 = NO_2$, $R_3 = H$
T-mNT: $R_1 = R_3 = H$, $R_2 = NO_2$ **T-35dNT**: $R_1 = H$, $R_2 = R_3 = NO_2$

Scheme S1. Synthesis of NO_2 substituted T-Phenazines.

Compound B To a solution of compound **A** (2 g, 3.07 mmol), palladium acetate ($Pd(OAC)_2$) (55.2 mg, 0.25 mmol), and triphenylphosphine (PPh_3) (165.6 mg) in 80 mL tetrahydrofuran (THF) and 20 mL isopropylamine (IPA), (triisopropylsilyl)acetylene (2.07 mL, 9.22 mmol) and copper iodide (CuI) (55.2 mg) were added. The reaction mixture was refluxed for 2.5 hours. After cooling it to room temperature, the reaction mixture was filtered through Celite with hot chloroform to remove reaction salts and catalysts, and the solvents were evaporated under reduced pressure. The crude compound was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane 3/7 to 1/1) to give the pure product as an orange solid (93 % yield). ^{1}H NMR ($CDCl_3$) δ 7.82 (s, 2H), 7.30 (s, 2H), 4.22 (t, 4H, J = 6.8 Hz), 1.96, (m, 4H), 1.55 (m, 4H), 1.5-1.2 (m, 60H), 0.89 (t, 6H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 154.71, 142.15, 141.96, 132.11, 123.60, 105.96, 104.35, 99.54, 69.16, 31.94, 29.65, 29.59, 29.41, 29.36, 28.73, 26.07, 22.70, 18.85, 11.57. LR-ESI-MS calcd for $C_{54}H_{88}N_2O_2Si_2$ m/z = 852.64, found m/z = 853.7 $[M+H]^+$

Compound C To a solution of compound **B** (1.96 g, 2.29 mmol) in 70 mL tetrahydrofuran (THF), tetrabutylammonium fluoride (TBAF) (2.17 g, 6.88 mmol) was added. The reaction mixture was stirred for 15 minutes at room temperature. After reaction, the reaction mixture was washed with water to remove remaining reaction reagent. The organic layer was collected, dried over sodium sulfate (Na_2SO_4), and filtered with chloroform. The solvent, after filtration, was evaporated under reduced pressure. The crude compound was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane 3/7 to 3/2) to give the pure product as a yellow solid (75 % yield). ^{1}H NMR ($CDCl_3$) δ 7.92 (s, 2H), 7.47 (s, 2H), 4.23 (t, 4H, J = 6.6 Hz), 3.73 (s, 2H),

1.96 (m, 4H), 1.54 (m, 4H), 1.5-1.2 (m, 24H), 0.89 (t, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ 155.23, 142.55, 141.48, 132.96, 122.65, 105.93, 84.92, 80.85, 69.50, 31.92, 29.61, 29.57, 29.36, 28.75, 26.02, 22.70, 14.14 (1 aliphatic peak not seen due to overlapping signals). LR-ESI-MS calcd for $C_{36}H_{48}N_2O_2$ m/z = 540.37, found m/z = 541.3 $[M+H]^+$

T-pNT To a solution of compound C (150 mg, 0.28 mmol), dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$) (2.0 mg, 0.0028 mmol) in 10 mL tetrhydrofuran and 2.5 mL triethylamine, 1-iodo-4-nitrobenzene (207.4 mg, 0.83 mmol) and copper iodide (0.5 mg, 0.0026 mmol) were added. The reaction mixture was refluxed for 2 hours. After cooling it to room temperature, the reaction mixture was filtered through Celite with hot chloroform to remove reaction salts and catalysts, and the solvent, after filtration, was evaporated under reduced pressure. The crude compound was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane 3/7 to CH_2Cl_2) to give the pure product as a yellow solid (70 % yield). ^{1}H NMR ($CDCl_3$) δ 8.30 (d, 4H, J = 8.8 Hz), 8.03 (s, 2H), 7.89 (d, 4H, J = 8.8 Hz), 7.46 (s, 2H), 4.27 (t, 4H, J = 6.4 Hz), 1.98 (m, 4H), 1.57 (m, 4H), 1.5-1.2 (m, 24H), 0.89 (t, 6H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 155.54, 147.29, 142.63, 141.26, 132.75, 132.69, 130.17, 123.69, 123.14, 105.83, 95.43, 92.20, 59.56, 53.43, 31.93, 29.62, 29.59, 29.36, 28.81, 26.07, 22.70, 14.12. LR-EI-MS calcd for $C_{48}H_{54}N_4O_6$ m/z = 782.40, found m/z = 782.5 $[M]^+$

T-mNT To a solution of compound C (150 mg, 0.28 mmol), dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$) (2.0 mg, 0.0028 mmol) in 10 mL tetrhydrofuran and 2.5 mL triethylamine, 1-iodo-3-nitrobenzene (208.7 mg, 0.83 mmol) and copper iodide (0.5 mg, 0.0026 mmol) were added. The reaction mixture was refluxed for 2 hours. After cooling it to room temperature, the reaction mixture was filtered through Celite with hot chloroform to remove reaction salts and catalysts, and the solvent, after filtration, was evaporated under reduced pressure. The crude compound was purified by basic alumina column chromatography (eluent: CH_2Cl_2/hexane 3/7 to 3/2) to give the pure product as a yellow solid (55 % yield). ^{1}H NMR ($CDCl_3$) δ 8.60 (s, 2H), 8.24 (d, 2H, J = 8 Hz), 8.03 (d, 2H, J = 7.6 Hz), 8.00 (s, 2H), 7.60 (t, 2H, J = 8 Hz), 7.47 (s, 2H), 4.28 (t, 4H, J = 6.4 Hz), 1.98 (m, 4H), 1.57 (m, 4H), 1.5-1.2 (m, 24H), 0.88 (t, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ 155.46, 148.22, 142.59, 141.28, 137.60, 132.55, 129.41, 126.89, 125.20, 123.27, 123.01, 105.88, 94.69, 89.61, 69.56, 31.93, 29.63, 29.59, 29.39, 29.37, 28.84, 26.08, 22.70, 14.12. LR-EI-MS calcd for $C_{48}H_{54}N_4O_6$ m/z = 782.40, found m/z = 782.5 $[M]^+$

T-34dNT To a solution of compound C (232 mg, 0.43 mmol), dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$) (3.0 mg, 0.0043 mmol) in 12 mL tetrhydrofuran and 3 mL triethylamine, 1-iodo-3,4-dinitrobenzene (379 mg, 1.29 mmol) and copper iodide (0.8 mg, 0.0042 mmol) were added. The reaction mixture was refluxed for 1.25 hours. After cooling it to room temperature, the reaction mixture was filtered through Celite with hot chloroform to remove reaction salts and catalysts, and the solvent, after filtration, was evaporated under reduced pressure. The crude compound was purified by basic alumina column chromatography (eluent: CH_2Cl_2/hexane 1/1 to 9/1) to give the pure product as a red solid (69 % yield). ^{1}H NMR ($CDCl_3$) δ 8.21 (s, 2H), 8.03 (m, 6H), 7.44 (s, 2H), 4.29 (t, 4H, J = 6.6 Hz), 1.99 (m, 4H), 1.58 (m, 4H), 1.5-1.2 (m, 24H), 0.89 (t, 6H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 155.92, 142.86, 141.22, 141.17, 135.76, 132.82, 129.90, 128.01, 125.51, 122.91, 105.64, 94.25, 93.18, 69.68, 31.93,

29.63, 29.59, 29.37, 28.81, 26.08, 22.71, 14.13 (1 aromatic peak and 1 aliphatic peak not seen due to overlapping signals). LR-EI-MS calcd for $C_{48}H_{52}N_6O_{10}$ *m/z* = 872.37, found *m/z* = 872.4 $[M]^+$

T-35dNT To a solution of compound **C** (250 mg, 0.463 mmol), dichlorobis(triphenyl-phosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$) (3.2 mg, 0.0046 mmol) in 20 mL of tetrahydrofuran and 5 mL of triethylamine (degassed with Argon), 1-iodo-3,5-dinitro-benzene (340 mg, 1.16 mmol) and CuI (8.8 mg, 0.0046 mmol) were added. The reaction mixture was refluxed for 30 minutes until a solid mass formed. The solids were filtered and washed with methanol. The pure product was obtained by silica gel column chromatography (CH_2Cl_2) followed by alumina column chromatography (CH_2Cl_2) in 35% yield. ^{1}H NMR (400MHz, $CDCl_3$, ppm) δ 9.05 (2H, t, *J*= 2.2 Hz), 8.88 (4H, d, *J*=2.0 Hz), 8.07 (2H, s), 7.49 (2H, s), 4.31 (4H, t, *J*= 6.6 Hz), 2.00 (4H, m), 1.58 (4H, m), 1.45-1.28 (24H, overlapping peaks), 0.88 (6H, t, *J*=6.8 Hz). ^{13}C (100 MHz, $CDCl_3$, ppm): 155.89, 148.56, 142.86, 141.19, 132.79, 131.60, 127.06, 122.79, 118.22, 105.67, 92.77, 92.54, 69.68, 31.90, 29.60, 29.56, 29.36, 29.34, 28.79, 26.07, 22.68, 14.10. LR-ESI-MS calcd for $C_{48}H_{52}N_6O_{10}$ *m/z* = 872.37, found *m/z* = 873.3 $[M+H]^+$

Organogelation: The suspension of a weighed amount of each compound in an organic solvent was heated in a screw-cap vial until the solid dissolved. After cooling to room temperature, gelation was considered successful if no flow was observed upon inverting the vial.

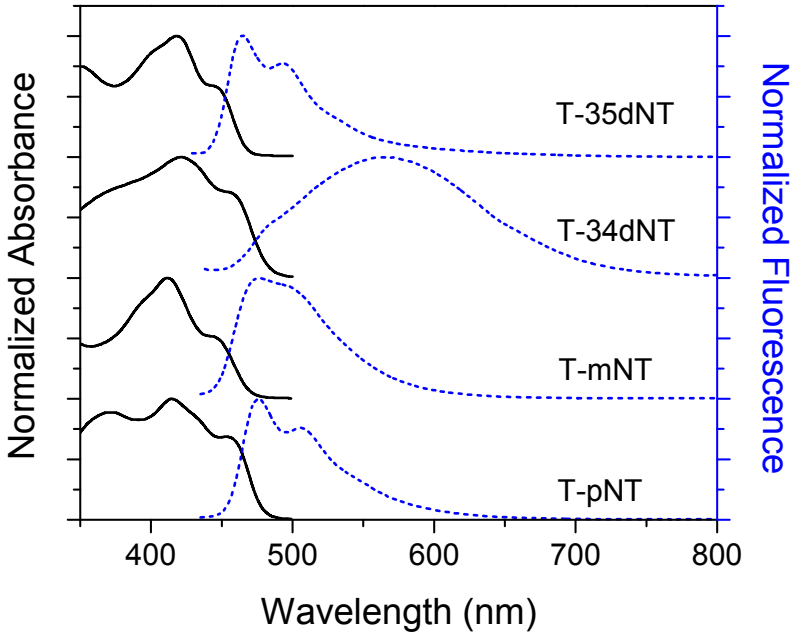


Figure S1. UV-vis absorption (solid line) and fluorescence (dashed line) spectra of T-phenazines in DCM. Excitation wavelength: 412 nm for **T-pNT** and **T-mNT**, and 422 nm for **T-34dNT** and **T-35dNT**.

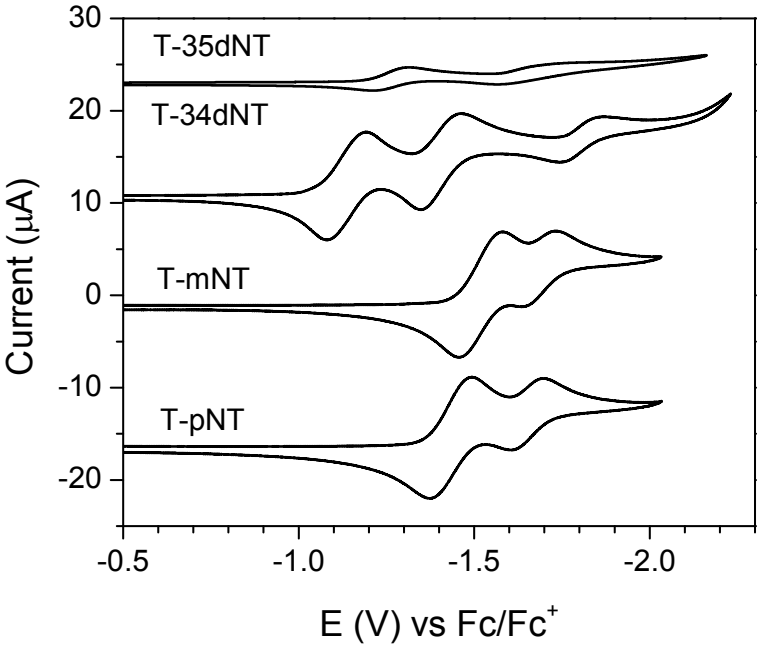


Figure S2. Cyclic voltammograms of NO_2 substituted T-phenazine molecules.

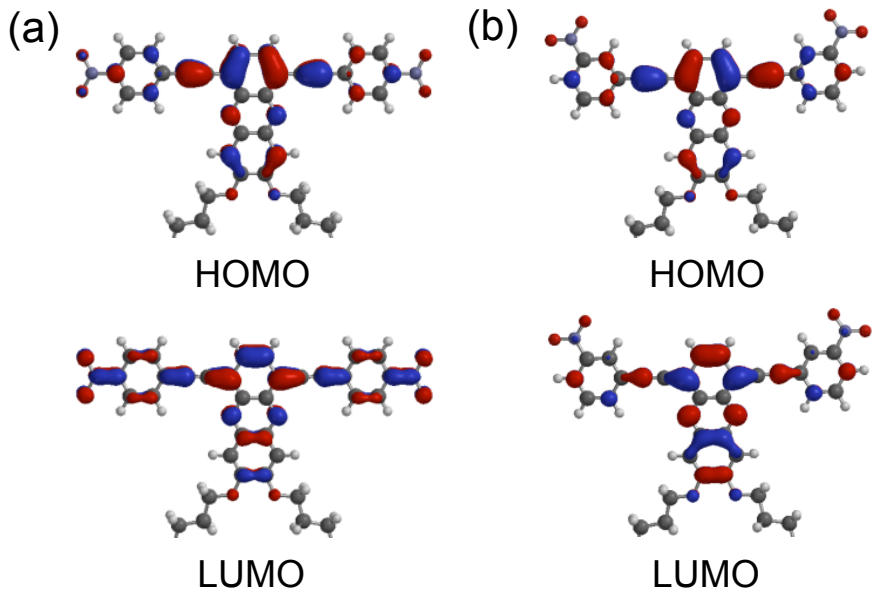


Figure S3. Frontier molecular orbital diagrams of (a) **T-pNT** and (b) **T-mNT**.

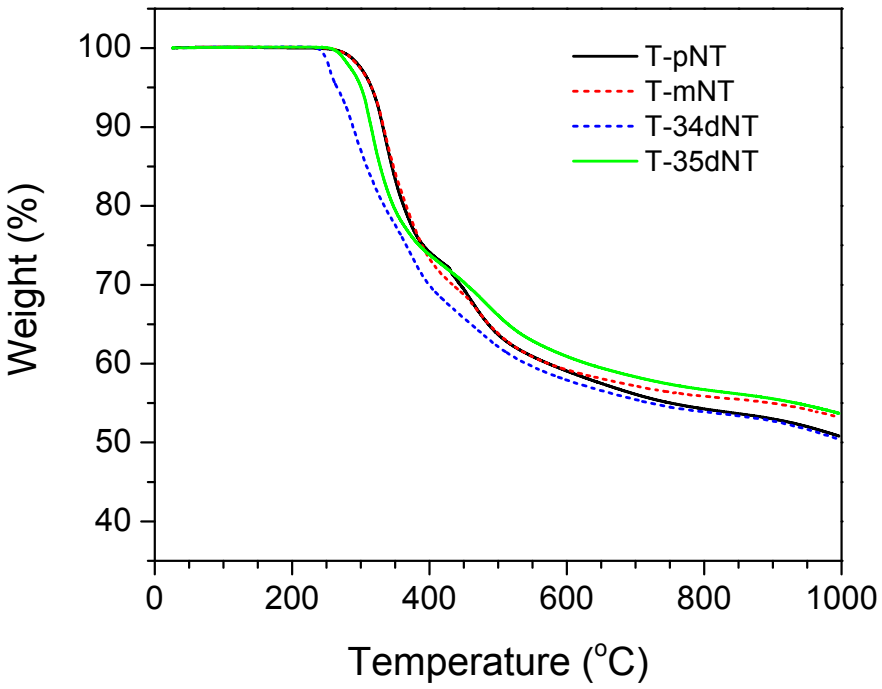


Figure S4. TGA thermograms of T-phenazine compounds.

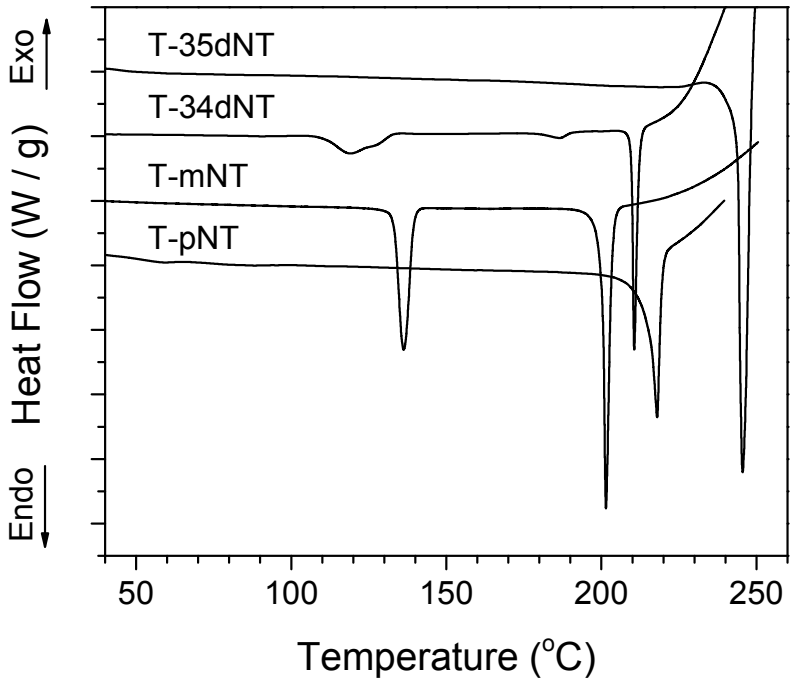


Figure S5. DSC thermograms of T-phenazine compounds.

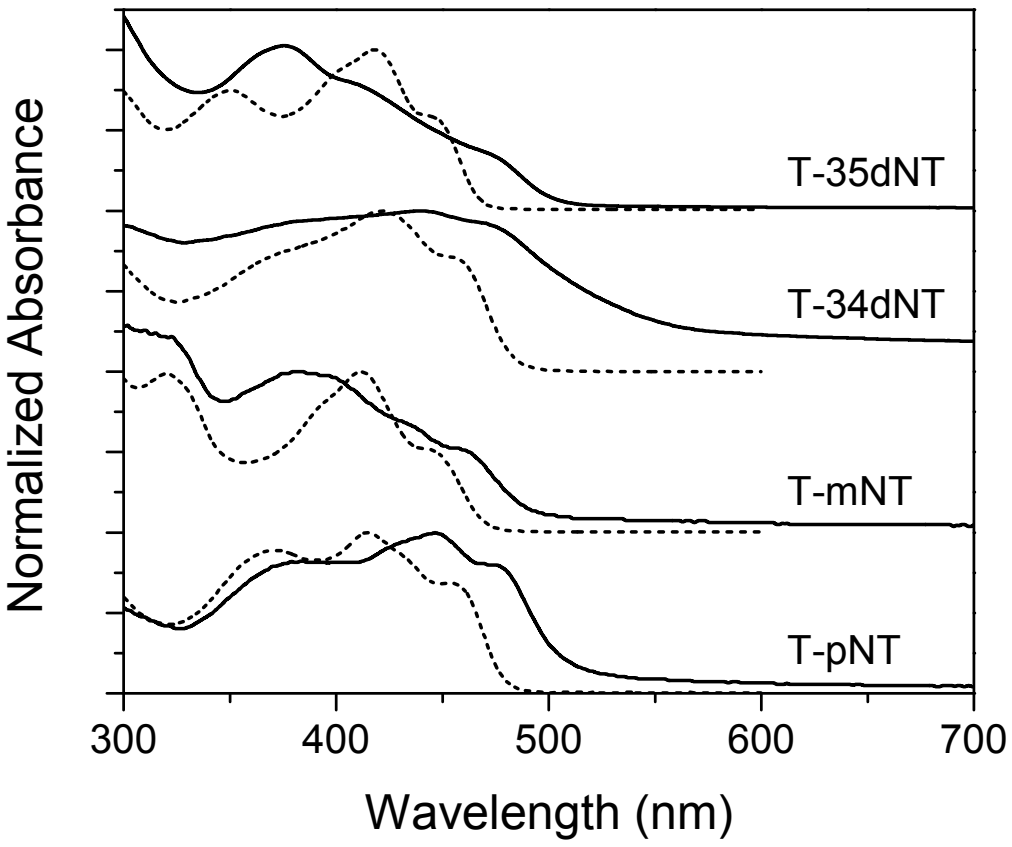


Figure S6. UV-vis spectra of T-phenazine compounds in solution (dashed line) and as films (solid line).

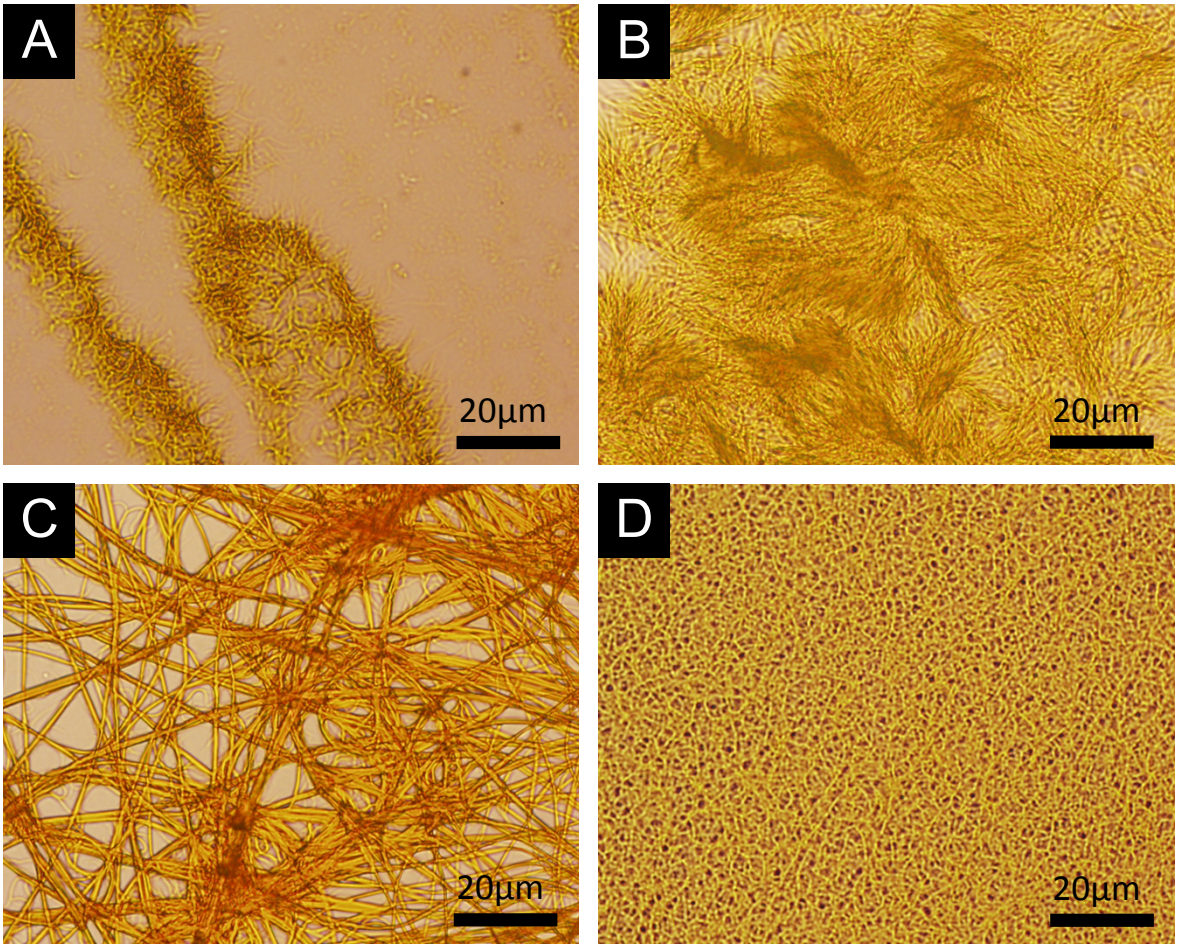


Figure S7. POM images of cast films from DCM solutions: (A) **T-pNT**, (B) **T-mNT**, (C) **T-34DNT**, and (D) **T-35DNT**.

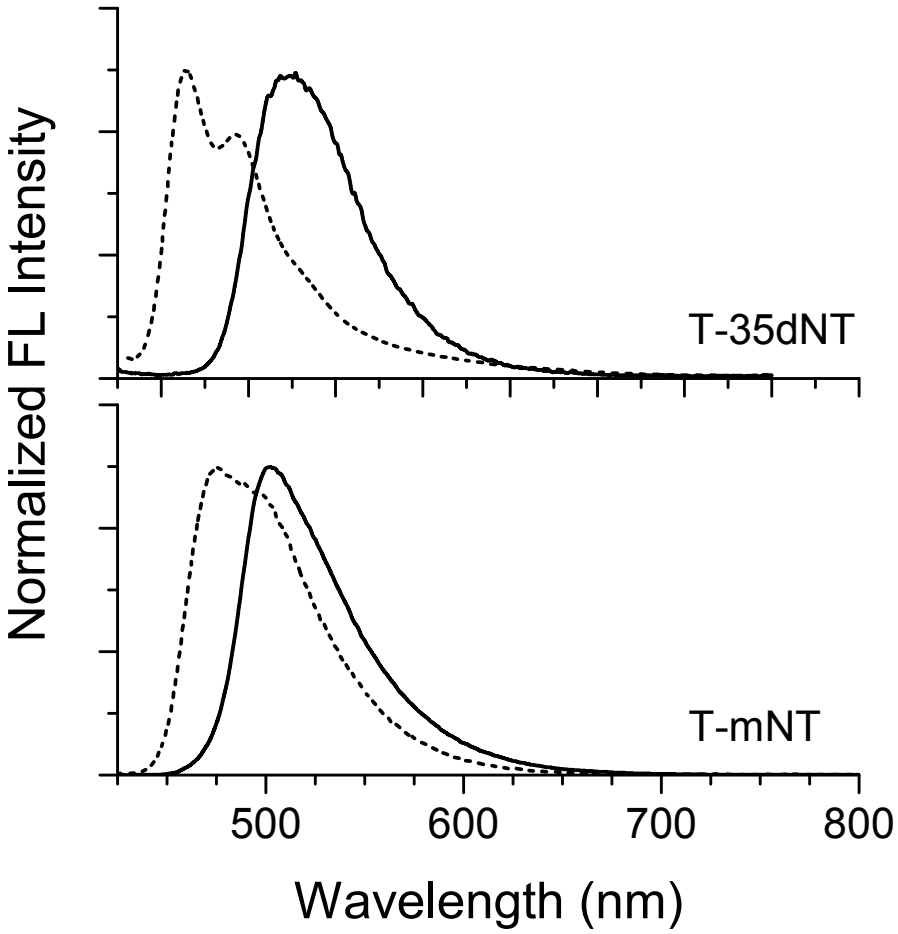


Figure S8. Fluorescence of AN gel (solid line) and DCM solution (dotted line). Gel concentration: **T-mNT** (5 mM) and **T-35dNT** (0.5 m M). λ_{ex} = 412 nm for **T-mNT** and 418 nm for **T-35dNT**.

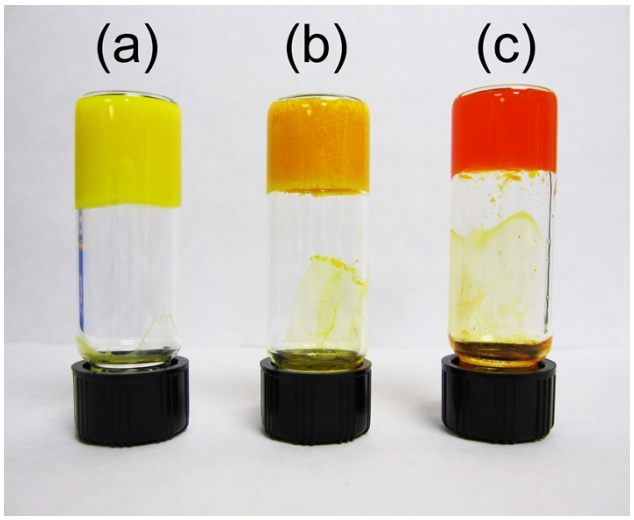


Figure S9. Pictures of **T-34dNT** gels: (a) in AN (7 mM), (b) in EA (10 mM), and (c) in cyclohexane (7 mM).

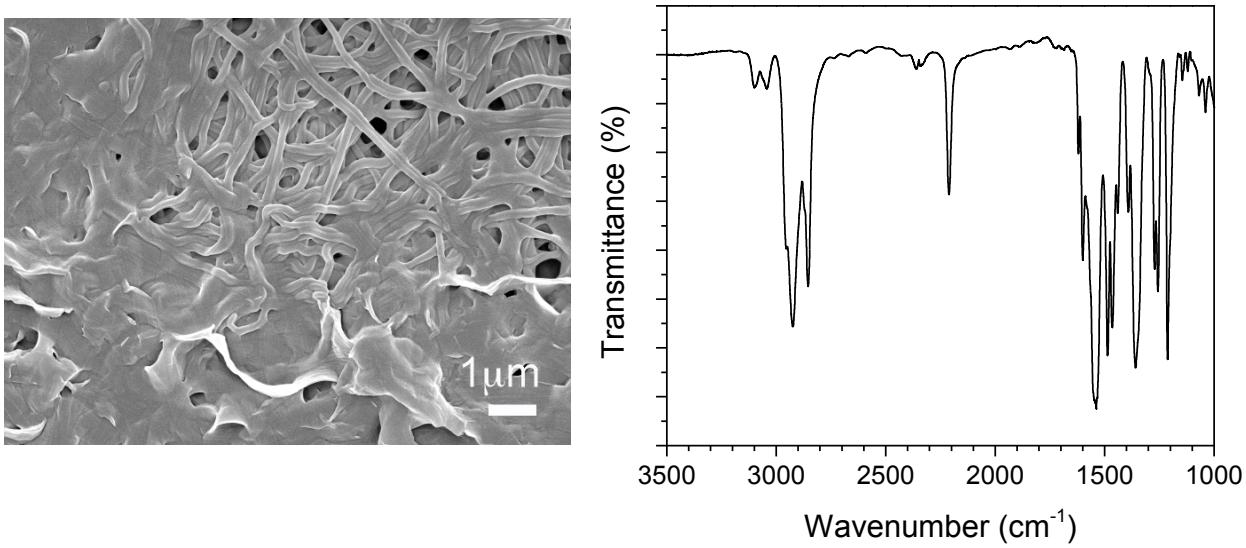


Figure S10. SEM image of xerogel of **T-34dNT** from AN gel dried for 1 week at ambient condition (left) and FT-IR spectrum of the corresponding sample (right).

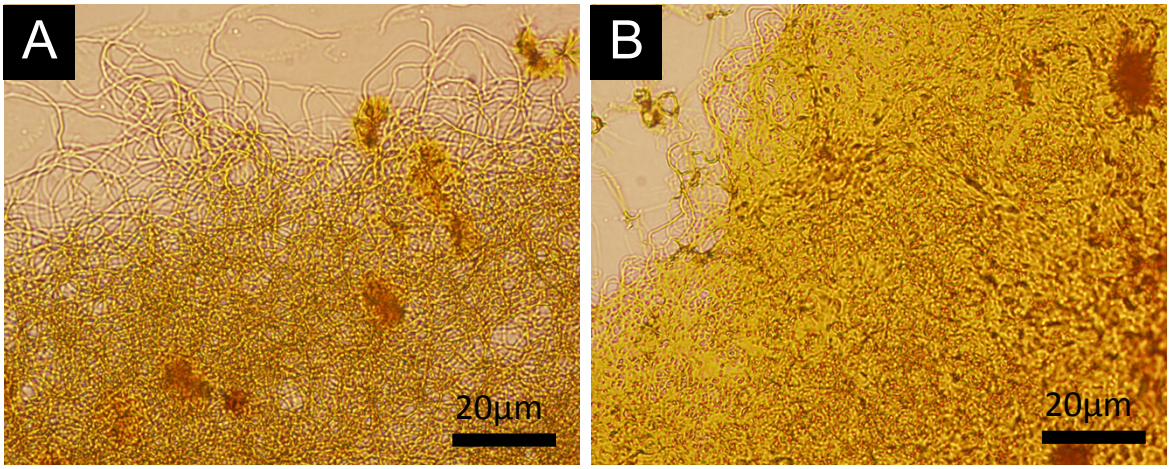


Figure S11. POM images of xerogel of **T-34dNT** from AN gel: (A) pristine and (B) dried for 1 week at ambient condition.

Table S1. Molar absorptivity (ε) and fluorescence quantum yield (Φ_F) in DCM.

	ε [$cm^{-1}M^{-1}$]	Φ_F [a]
T-pNT	5.8×10^4 (415 nm), 3.9×10^4 (454 nm)	13%
T-mNT	5.5×10^4 (412 nm), 2.8×10^4 (446 nm)	6.5%
T-34dNT	4.0×10^4 (422 nm), 2.8×10^4 (458 nm)	4.1%
T-35dNT	4.4×10^4 (418 nm), 2.6×10^4 (444 nm)	0.8%

[a] Measured with diphenyl anthracene as a standard ($\Phi_F = 0.90$).

Table S2. Thermal properties of the T-phenazines.

	T-pNT	**T-mNT**	**T-34dNT**	**T-35dNT**
T_d (°C)	315.6	316.0	265.6	300.4
T_m (°C) (ΔH_m (J/g))	217.99 (80.01)	136.29 (45.48) 201.48 (61.62)	119.03 (30.08) 210.58 (50.37)	245.54 (48.96)

Table S3. Gelation properties of T-Phenazine compounds in select organic solvents.

Solvent	T-pNT	T-mNT	T-34dNT	T-35dNT
Cyclohexane	NS	PG	G (7mM, 40°C)	G (1mM, 32°C)
Hexane	NS	NS	NS	NS
Decane	ppt	G (2mM, 50°C)	ppt	NS
Toluene	S	S	ppt	G (rapid cooling, 3mM, 29°C)
Ethyl Acetate	ppt	ppt	G (10mM, 60°C)	G (1mM, 31°C)
Tetrahydrofuran	ppt	S	S	S
1,1,1-Trichloroethane	ppt	S	ppt	G (2mM, 30°C)
1,2-Dichloroethane	ppt	S	S	G (3mM, 45°C)
CCl_4	ppt	ppt	PG	G (2mM, 31°C)
Ethanol	ppt	G (3mM, 31°C)	ppt	ppt
Propanol	ppt	G (3mM, 37°C)	ppt	NS
Acetonitrile	ppt	G (5mM, 48°C)	G (2mM, 40°C)	G (0.5mM)[a]

Abbreviations: **G**, gel; **PG**, partial gel; **ppt**, precipitation upon cooling; **S**, soluble after cooling; **NS**, not soluble. Critical Gelator Concentration (CGC) is shown in parentheses. For gels, T_g, is provided. [a] gel is not stable. At lower concentration, precipitate formed.

References

1. D.-C. Lee, B. Cao, K. Jang and P. M. Forster, J. Mater. Chem. 2010, 20, 867-873.
2. R. S. Kapil, J. Chem. Soc. 1959, 4127-4128.