Supplementary Information for:

Nanofibers of asymmetrically substituted bisphenazine through organogelation and their acid sensing properties

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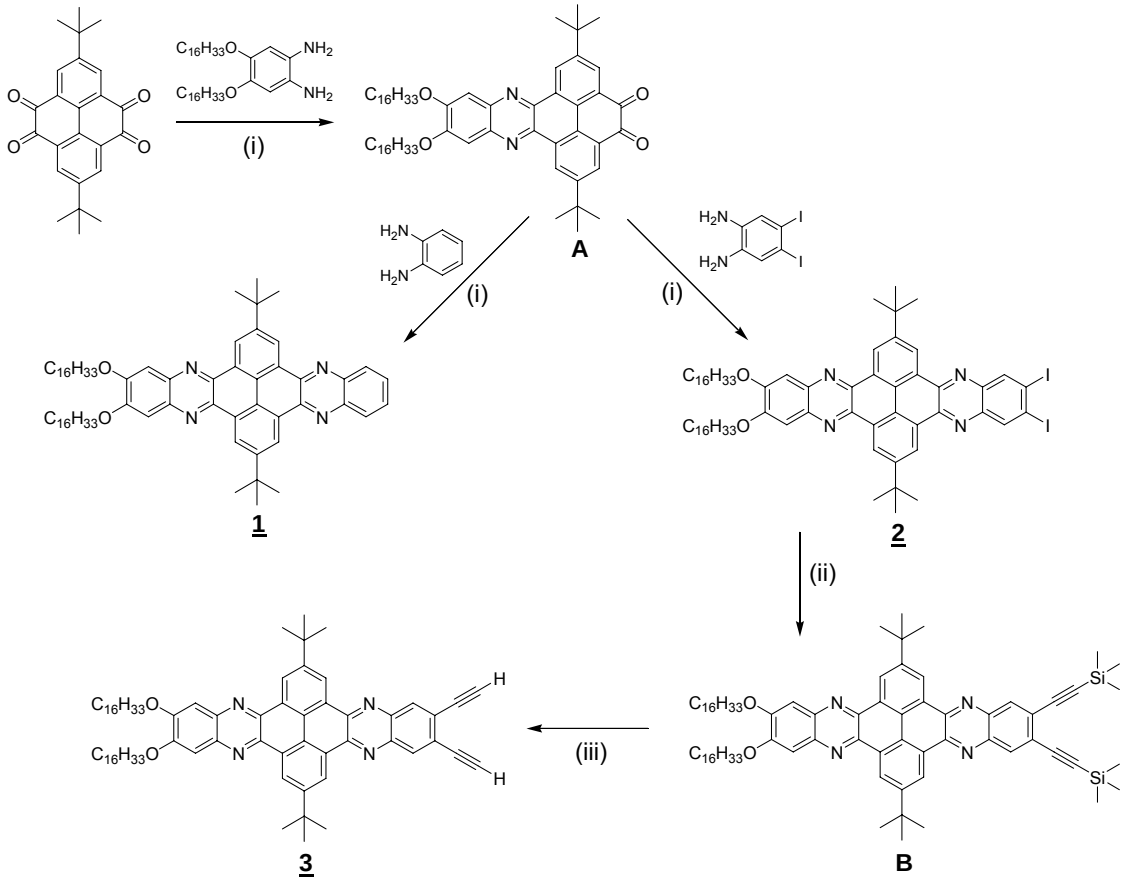
General Instrumentation: All ^{1}H-NMR and ^{13}C-NMR were obtained at 25°C on a Varian Gemini 400 MHz spectrometer using deutrated chloroform ($CDCl_3$) containing tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded at room temperature with a spectral resolution of 2 cm^{-1} using a Shimadzu IR Prestige-21 FTIR spectrometer. For solution IR of compound **3**, a 0.32mM solution in CCl_4 was used with a KBr cell with 1mm Teflon spacer. The mass spectra were recorded at the University of North Carolina Chapel Hill with a Micromass Quattro II triple quadrupole mass spectrometer equipped with a nano-electrospray ionization source.

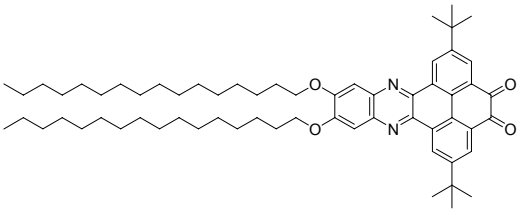
1. Synthesis and characterization of intermediates and target products 1, 2, and 3

All chemicals and solvents were purchased from commercial sources and used as received. 2,7-Di-*tert*-butylpyrene-4,5,9,10-tetraone,[1] 1,2-diamino-4,5-dihexadecoxybenzene,[2,3] and 1,2-diamino-4,5-diiodobenzene[4] were all synthesized according to the literature.



Scheme S1. Synthetic routes to **1**, **2**, and **3**. Reagents and conditions: (i) $CHCl_3$ / glacial acetic acid, reflux; (ii) Sonogashira coupling: $Pd(TPP)_2Cl_2$, CuI, TEA, and THF; (iii) CH_2Cl_2 / methanolic KOH, 45°C.

Compound A



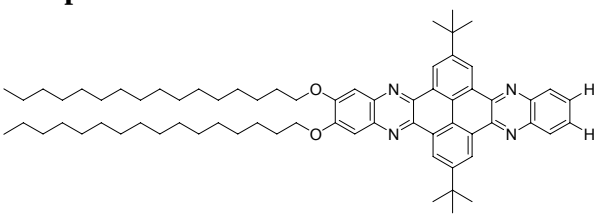
2,7-Di-*tert*-butylpyrene-4,5,9,10-tetraone (0.981 g, 2.62 mmol) was dissolved in 132 mL of chloroform and 33 mL of glacial acetic acid. 1,2-Diamino-4,5-dihexadecoxybenzene (0.883 g, 1.50 mmol) was added at once and the mixture was refluxed for 2 hrs under a positive N_2 flow. The reaction mixture was cooled to room temperature, and washed with H_2O and 10% $NaOH_{(aq)}$. The organic layer was dried over Na_2SO_4. Na_2SO_4 was filtered out and the filter cake was rinsed with hot methylene chloride. The solvent was removed under vacuum to yield the crude product which was purified by column chromatography (CH_2Cl_2/hexane 1/1 v/v). The pure product was obtained as a yellow solid (72%).

^{1}H-NMR: ($CDCl_3$) δ [ppm]: 9.52 (d, *J* = 2.0 Hz, 2H, Ar-H), 8.51 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 4.25 (t, *J* = 6.6 Hz, 4H, -CH_2-), 2.04 – 1.97 (m, 4H, -CH_2-), 1.58 (s, 18H, -CH_3), 1.49 – 1.26 (m, 52H, -CH_2-), 0.87 (t, *J* = 6.8 Hz, 6H, -CH_3)

^{13}C-NMR: ($CDCl_3$) δ [ppm]: 180.56, 153.97, 152.02, 140.22, 138.85, 130.66, 129.90, 129.44, 129.14, 127.64, 106.62, 69.35, 35.59, 31.93, 31.28, 29.74, 29.68, 29.66, 29.42, 29.38, 28.90, 26.10, 22.70, 14.13 (5 alkyl peaks not seen due to overlapping signals)

$[M+H]^+$: Calcd 927.69, Found 927.7

Compound 1



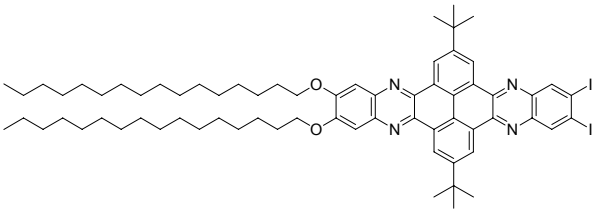
Compound **A** (0.200 g, 0.216 mmol) was dissolved in 52 mL chloroform and 17 mL glacial acetic acid. To that solution, 1,2-diaminobenzene (0.025 g, 0.231 mmol) in acetic acid/chloroform was added at once. The reaction mixture was refluxed for 3 hrs under a positive N_2 flow. The mixture was cooled and washed with H_2O, 10% $NaOH_{(aq)}$, and saturated $NaCl_{(aq)}$. The organic layer was dried over Na_2SO_4, and filtered. The solvent was removed under vacuum to yield the crude product as an orange/yellow solid which was purified by column chromatography (CH_2Cl_2/hexane 2/3 v/v). Pure product was obtained as a yellow solid (80%). **m.p. (DSC):** 85.10 ºC

^{1}H-NMR: ($CDCl_3$) δ [ppm]: 9.77 (d, *J* = 2.0, 2H, Ar-H), 9.75 (d, *J* = 2.0, 2H, Ar-H), 8.44 – 8.41 (m, 2H, Ar-H), 7.90 – 7.87 (m, 2H, Ar-H), 7.61 (s, 2H, Ar-H), 4.32 (t, *J* = 6.6, 4H, -CH_2), 2.05 – 1.98 (m, 4H, -CH_2), 1.76 (s, 18H, -CH_3), 1.64 – 1.56 (m, 4H, -CH_2), 1.50 – 1.26 (m, 48H, -CH_2), 0.87 (t, *J* = 6.8, 6H, -CH_3)

^{13}C-NMR: ($CDCl_3$) δ [ppm]: 153.37, 150.56, 143.24, 142.24, 140.43, 139.99, 129.71, 129.56, 129.26, 125.21, 123.76, 123.70, 106.93, 69.26, 35.90, 31.94, 31.91, 29.75, 29.68, 29.46, 29.39, 28.96, 26.13, 22.71, 14.14 (1 aromatic and 6 alkyl peaks not seen due to overlapping signals)

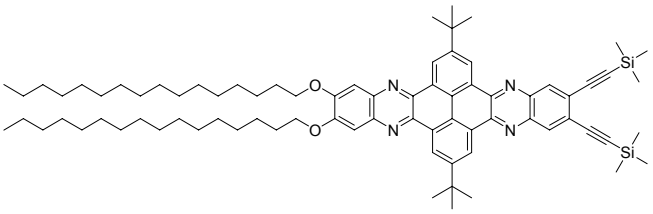
$[M+H]^+$: Calcd 999.74, Found 999.8

Compound 2



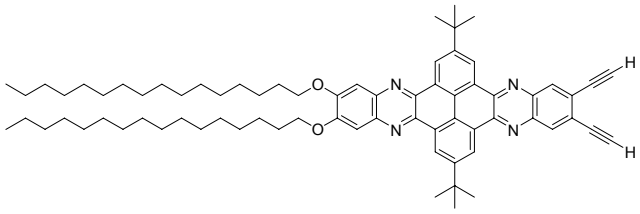
Compound **A** (0.900 g, 0.97 mmol) was dissolved in 200 mL chloroform and 62 mL glacial acetic acid. To that solution, 1,2-diamino-4,5-diiodobenzene (0.349 g, 0.97 mmol) was added at once. The reaction mixture was refluxed overnight under a positive N_2 flow. The mixture was washed with H_2O and 10% $NaOH_{(aq)}$. The organic layer was dried over Na_2SO_4, and filtered. The solvent was removed under vacuum to yield the crude product which was purified by column chromatography (CH_2Cl_2/hexane 2/3 v/v). The pure product was obtained as a yellow solid (71%). **m.p. (DSC):** 105.43 ºC
^{1}H-NMR: ($CDCl_3$) δ [ppm]: 9.70 (d, *J* = 2.0 Hz, 2H, Ar-H), 9.59 (d, *J* = 2.0 Hz, 2H, Ar-H), 8.86 (s, 2H, Ar-H),7.53 (s, 2H, Ar-H), 4.29 (t, *J* = 6.6 Hz, 4H, -CH_2-), 2.04 – 1.97 (m, 4H, -CH_2-), 1.76 (s, 18H, -CH_3), 1.63 – 1.58 (m, 4H, -CH_2-), 1.49 – 1.26 (m, 48H, -CH_2-), 0.87 (t, *J* = 7.0 Hz, 6H, -CH_3)
Significant ^{13}C-NMR results were not obtained due to limited solubility.
[M+H]$^+$: Calcd 1251.53, Found 1251.5

Compound B



$Pd(TPP)_2Cl_2$ (11.4 mg, 0.016 mmol) and compound **2** (0.202 g, 0.162 mmol) were suspended in 32 mL of degassed anhydrous THF. To the mixture, CuI (1.5 mg, 7.88 mmol), 4.5 mL of degassed TEA, and 0.07 mL (0.495 mmol) of trimethylsilylacetylene were added. The mixture was heated to 70 ^{o}C overnight under a positive N_2 flow. The mixture was filtered through a bed of Celite® using hot methylene chloride. The filtrate was concentrated under vacuum to yield the crude product as a brown oil which was purified by column chromatography (CH_2Cl_2/hexane 2/3 v/v). Pure product was obtained as a yellow solid (87%).
^{1}H-NMR: ($CDCl_3$) δ [ppm]: 9.61 (d, *J* = 2.0 Hz, 2H, Ar-H), 9.58 (d, *J* = 2.4 Hz, 2H, Ar-H), 8.44 (s, 2H, Ar-H), 7.34 (s, 2H, Ar-H), 4.21 (t, *J* = 6.6 Hz, 4H, -CH_2-), 1.99 – 1.92 (m, 4H, -CH_2-), 1.76 (s, 18H, -CH_3), 1.61 – 1.54 (m, 4H, -CH_2-), 1.50 – 1.26 (m, 48H, -CH_2-), 0.87 (t, *J* = 6.8 Hz, 6H, -CH_3)
^{13}C-NMR: ($CDCl_3$) δ [ppm]: 153.33, 150.59, 144.01, 141.39, 140.23, 139.94, 133.60, 129.70, 128.86, 125.98, 125.22, 124.13, 123.89, 106.83, 102.63, 100.85, 69.22, 35.86, 31.94, 31.85, 29.76, 29.74, 29.68, 29.47, 29.39, 28.96, 26.12, 22.70, 14.14, 0.03 (5 alkyl peaks not seen due to overlapping signals)
[M+H]$^+$: Calcd 1191.82, Found 1192.9

Compound 3



Compound **B** (0.122 g, 0.113 mmol) was dissolved in 56 mL of CH_2Cl_2. KOH (0.020 g, 0.356 mmol) in 5 mL of methanol was added to the solution. The mixture was heated to 45 ^oC for 6 hrs, cooled to room temperature, and filtered through a bed of silica gel followed by rinsing with hot chloroform. The filtrate was concentrated under vacuum to yield the crude product as an orange/brown oil which was purified by two times of column chromatography with $CHCl_3$ as an eluent. Pure product was obtained as a yellow solid (57%). **m.p. (DSC):** 102.37 ºC

^{1}H-NMR: ($CDCl_3$) δ [ppm]: 9.66 (d, J = 2.0 Hz, 2H, Ar-H), 9.60 (d, J = 2.4 Hz, 2H, Ar-H), 8.51 (s, 2H, Ar-H), 7.50 (s, 2H, Ar-H), 4.29 (t, J = 6.6 Hz, 4H, -CH_2-), 3.51 (s, 2H, -C≡C-H), 2.03 – 1.96 (m, 4H, -CH_2-), 1.75 (s, 18H, -CH_3), 1.63 – 1.96 (m, 4H, -CH_2-), 1.49 – 1.26 (m, 48H, -CH_2-), 0.87 (t, J = 6.8 Hz, 6H, -CH_3)

^{13}C-NMR: ($CDCl_3$) δ [ppm]: 153.38, 150.62, 144.27, 141.34, 140.14, 139.97, 134.15, 129.68, 128.66, 125.23, 124.96, 124.31, 123.94, 106.83, 82.93, 81.39, 69.24, 35.88, 31.94, 31.86, 29.76, 29.74, 29.69, 29.48, 29.39, 28.96, 26.13, 22.70, 14.14 (5 alkyl peaks not seen due to overlapping signals)

$[M+Na]^+$: Calcd 1069.74, Found: 1069.8

2. Gelling ability of 1, 2, and 3

Gels were prepared by weighing a specified amount of compound (generally 1 wt%) and solvent into a small screw-cap vial. The suspension was warmed until a homogeneous solution was obtained. The vial was then left undisturbed to cool to room temperature. Gelation was confirmed by the absence of flow under gravity when the vial was inverted.

Table S1. Gelling abilities of **1**, **2**, and **3** at room temperature

Solvent [a]	***1***[b]	***2***[b]	***3***[b]
Cyclohexane	PPT	NS	NS
Decane	PPT	PG	1.3[c], TR
Ethyl acetate	NS	NS	NS
Hexadecane	PPT	PG	1.0[c], TR
Hexane	NS	NS	PPT
Toluene	S	PPT	PPT
CCl_4	S	S	S
DCE	PPT	NS	PPT
TCE	PG	S	10.0[c], OP
TCTFE	NS	NS	NS
THF	PPT	PPT	S

[a] TCE – 1,1,1-trichloroethane, DCE – 1,2-dichloroethane, TCTFE – 1,1,2-trichloro-1,2,2-trifluoroethane

[b] G – gel, PG – partial gel, PPT – precipitate, NS – not soluble, S – solution at room temperature, OP – opaque, TR – transparent
[c] Critical gel concentration (CGC) in millimolar (mM)

3. Procedure for measurement of T_{gel}

The gelation temperature (T_{gel}) of gels of **3** formed in decane, hexadecane, and 1,1,1-trichloroethane were determined using the 'inverse flow' method. Gels were formed as previously described and placed upside down in a temperature regulated H_2O bath (decane and TCE) or a silicon oil bath (hexadecane). The temperature at which the gel fell from the bottom of the vial was taken as T_{gel} for that sample. In the case of the hexadecane gel, the T_{gel} was well beyond the range of the regulated H_2O bath. Therefore, an approximate T_{gel} was obtained using a silicon oil bath.

4. Sample preparation for SEM characterization and additional SEM images of the xerogel of 3

SEM samples were prepared by slow drying of the organogel of compound **3** in decane (1.3 mM) or TCE (10 mM) on a silicon wafer at ambient conditions. All SEM images were obtained using a Hitachi S-4700 scanning electron microscope with an accelerating voltage of 2kV. Silicon wafers containing samples were mounted on stainless steel stubs with carbon tape. Before imaging, all samples were sputter-coated with 2.3 nm of gold.

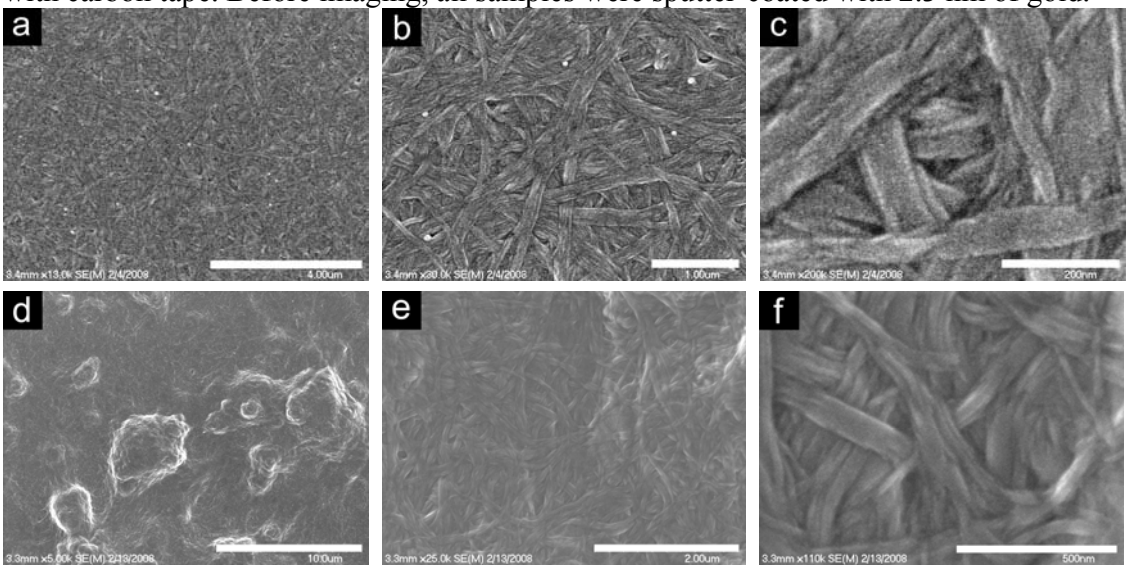


Figure S1. SEM images of the xerogel of **3** from decane gel (1.3 mM, images (a), (b), and (c), scale bars: (a) 4 μm, (b) 1 μm, and (c) 200 nm) and from TCE gel (10 mM, images (d), (e), and (f), scale bars: (d) 10 μm, (e) 2 μm, and (f) 500 nm).

5. X-ray diffraction pattern of the xerogel of 3

X-ray diffraction analyses were carried out on an X'Pert PRO PANalytical diffractometer at 25 ^{o}C using Cu (40 kV, 40 mA) radiation.

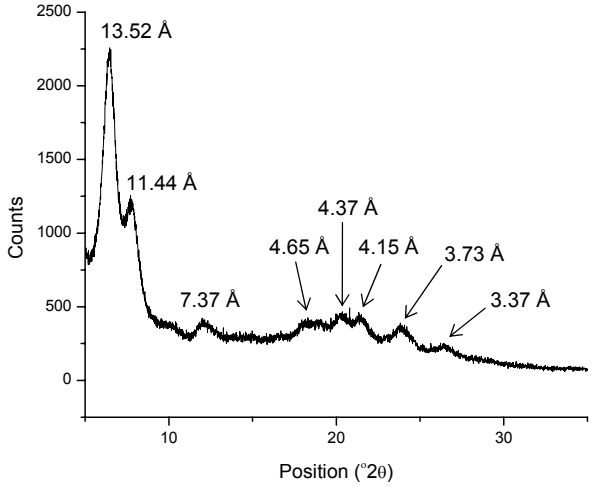


Figure S2. X-ray diffraction pattern for the xerogel of **3** from TCE.

6. Acid sensitivity of xerogel and amorphous film of 3

For UV-Vis spectroscopy, the xerogel obtained from the decane gel was used due to a lower gel concentration. Absorbance of the xerogel from the TCE gel exceeded the instrument limit. However, for visual identification of color change, the xerogel from TCE was used. For a control experiment, a cast film of **3** was prepared by dropping a homogeneous solution of **3** in TCE on a hot microscope slide and rapidly evaporating the solvent. The xerogel film was obtained by drying the gel of **3** on a microscope slide under ambient conditions for 1 hour. The films were placed in Petri dishes (volume = ca. 127 cm^3) containing one drop of trifluoroacetic acid (TFA), and the dish was immediately covered. Color changes of the films were observed by visual inspection.

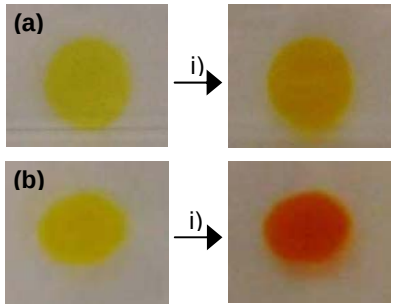


Figure S3. Cast film from rapid evaporation of TCE (a) and xerogel film (b) of **3** before and after i) exposure to the vapor of TFA for a few seconds. In the case of the cast film, extended exposure to the vapor of TFA did not change the color of the film.

References

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