Supplementary Information for:

Self-Assembly of Halogen Substituted Phenazines
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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 deuterated chloroform (CDCl$_3$) containing tetramethylsilane (TMS) as an internal standard. The mass spectra were recorded at the University of Illinois at Chicago. Differential Scanning Calorimetric (DSC) analyses were performed under nitrogen flow at heating and cooling rates of 10 °C/min using a TA instrument 2100 DSC. The UV-vis absorption spectra were collected on a Shimadzu UV-2450 UV-vis spectrophotometer. SEM images were obtained on a Jeol JSM-5600 scanning electron microscope. Before imaging, all samples were sputter-coated (50 mA, 60 sec) with a thin layer of gold to prevent charging. Accelerating voltages and working distances are specified with each image. A TECNAI-G2-F30 transmission electron microscope with a 300 KeV Schottky field emission gun was used to characterize the morphology and atomic structure of the molecules under the conventional diffraction contrast (bright-field, BF) and Z-contrast (scanning transmission electron microscope, STEM) modes. The samples were prepared on a 3 mm diameter carbon-coated copper grid. For High-resolution transmission electron microscopy (HRTEM), many-beam condition was used to characterize the atomic structure under the phase-contrast (HRTEM) mode. X-ray diffraction analyses were carried out on an X’Pert PRO PANalytical diffractometer at 25 °C using Cu-Kα radiation ($\lambda = 1.54$ Å, 40 KV, 40 mA).

1. **Synthesis and characterization of compounds 1-6**

All chemicals and solvents were purchased from commercial sources and used as received. 1,2-Diamino-4,5-dibromobenzene,$^1$ 1,2-diamino-3,6-dibromobenzene,$^2$ and 1,2-diamino-4,5-diiodobenzene$^3$ were all synthesized according to the literature.

**Compound 1**

1,2-Diaminobenzene (100 mg, 0.93 mmol) was dissolved in 20 mL absolute ethanol. 2,5-Dihydroxyl-1,4-benzoquinone (130 mg, 0.93 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N$_2$ flow. The reaction mixture was cooled slightly. Without purification of the intermediate, after evaporating the solvent, the crude solid was dissolved in 20 mL dimethylformamide (DMF), followed by addition of K$_2$CO$_3$ (447 mg, 3.23 mmol). Then bromodecane (616 mg, 2.79 mmol) was added and the mixture was maintained at 60 °C for 24 hrs with continuous stirring. The mixture was cooled down to room temperature and poured into 200 mL of H$_2$O, filtered and washed thoroughly with H$_2$O. It was then dried over anhydrous sodium sulfate. The product was purified by silica gel column chromatography (CH$_2$Cl$_2$/Hexane 1/1 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 58%).

$^1$H NMR (CDCl$_3$) δ 8.14 (m, 2H), 7.74 (m, 2H), 7.35 (s, 2H), 4.23 (t, 4H, $J = 6.6$ Hz), 1.96 (m, 4H), 1.54 (m, 4H), 1.46-1.20 (m, 24H), 0.89 (t, 6H, $J = 6.8$ Hz).

$^{13}$C NMR (CDCl$_3$) δ 154.48, 142.01, 141.84, 128.81, 105.54, 69.30, 31.92, 29.62, 29.58, 29.37, 29.36, 28.73, 26.05, 22.70, 14.12 (1 aromatic peak not seen due to overlapping signals).

[M+H]$^+$: Calcd 493.37; Found 493.3.

**Compound 2**

1,2-Diamino-4,5-difluorobenzene (50 mg, 0.35 mmol) was dissolved in 7 mL absolute ethanol. 2,5-Dihydroxyl-1,4-benzoquinone (49 mg, 0.35 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N$_2$ flow. The reaction mixture was cooled slightly. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in
8 mL DMF, followed by addition of K₂CO₃ (168 mg, 1.23 mmol). Then bromodecane (231 mg, 1.05 mmol) was added and the mixture was maintained at 60 °C for 24 hrs with continuous stirring. The mixture was cooled down to room temperature and poured into 80 mL of H₂O, filtered and washed thoroughly with H₂O. It was then dried over anhydrous sodium sulfate. The product was purified by silica gel column chromatography (CH₂Cl₂/Hexane 1/1 v/v). The pure product was obtained as a white solid. (Two-step yield: 68%).

^{1}H NMR (CDCl₃) δ 7.84 (t, 2H, J = 9.6 Hz), 7.30 (s, 2H), 4.22 (t, 4H, J = 6.6 Hz), 1.96 (m, 4H), 1.54 (m, 4H), 1.46-1.20 (m, 24H), 0.88 (t, 6H, J = 6.6 Hz).

^{13}C NMR (CDCl₃) δ 154.75, dd (153.56, 153.37, 151.00, 150.80), 141.88, t (139.02, 138.96, 138.91), q (113.65, 113.58, 113.52, 113.45), 105.28, 69.39, 31.93, 29.62, 29.58, 29.36, 28.72, 26.04, 22.70, 14.12 (1 aliphatic peak not seen due to overlapping signals).

[M+H]^+: Calcd 529.35; Found 529.3.

**Compound 3**

1,2-Diamino-4,5-dichlorobenzene (177 mg, 1 mmol) was dissolved in 25 mL absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (140 mg, 1 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N₂ flow. The reaction mixture was cooled slightly. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 20 mL DMF, followed by addition of K₂CO₃ (493 mg, 3.5 mmol). Then bromodecane (676 mg, 3.06 mmol) was added and the mixture was maintained at 60 °C for 24 hrs with continuous stirring. The mixture was cooled down to room temperature and poured into 200 mL of H₂O, filtered and washed thoroughly with H₂O. It was then dried over anhydrous sodium sulfate. The product was purified by silica gel column chromatography (CH₂Cl₂/Hexane 1/2 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 44%).

^{1}H NMR (CDCl₃) δ 8.21 (s, 2H), 7.25 (s, 2H), 4.21 (t, 4H, J = 6.6 Hz), 1.96 (m, 4H), 1.54 (m, 4H), 1.46-1.20 (m, 24H), 0.89 (t, 6H, J = 6.8 Hz).

^{13}C NMR (CDCl₃) δ 154.98, 142.16, 139.81, 132.75, 128.90, 105.10, 69.31, 31.96, 29.68, 29.64, 29.45, 29.41, 28.80, 26.08, 22.73, 14.14.

[M+H]^+: Calcd 561.29; Found 561.5.

**Compound 4**

1,2-Diamino-4,5-dibromobenzene (500 mg, 1.88 mmol) was dissolved in 40 mL absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (260 mg, 1.88 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N₂ flow. The reaction mixture was cooled slightly. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 40 mL DMF, followed by addition of K₂CO₃ (910 mg, 6.5 mmol). Then bromodecane (1.25 g, 5.64 mmol) was added and the mixture was maintained at 60 °C for 24 hrs with continuous stirring. The mixture was cooled down to room temperature and poured into H₂O, filtered and washed thoroughly with H₂O. It was then dried over anhydrous sodium sulfate. The product was purified by silica gel column chromatography (CH₂Cl₂/Hexane 1/2 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 57%).

^{1}H NMR (CDCl₃) δ 8.45 (s, 2H), 7.27 (s, 2H), 4.22 (t, 4H, J = 6.6 Hz), 1.95 (m, 4H), 1.54 (m, 4H), 1.46-1.20 (m, 24H), 0.88 (t, 6H, J = 7.0 Hz).

^{13}C NMR (CDCl₃) δ 155.28, 142.58, 140.72, 132.59, 124.97, 105.32, 69.44, 31.92, 29.63, 29.58, 29.36, 28.71, 26.03, 22.70, 14.12 (1 aliphatic peak not seen due to overlapping signals).

[M]^+: Calcd 648.19; Found 648.3.
**Compound 5**

1,2-Diamino-4,5-diiodobenzene (366 mg, 1.02 mmol) was dissolved in 25 mL absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (143 mg, 1.02 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N₂ flow. The reaction mixture was cooled slightly. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 20 mL DMF, followed by addition of K₂CO₃ (493 mg, 3.5 mmol). Then bromodecane (676 mg, 3.06 mmol) was added and the mixture was maintained at 60 °C for 24 hrs with continuous stirring. The mixture was cooled down to room temperature and poured into 200 mL of H₂O, filtered and washed thoroughly with H₂O. It was then dried over anhydrous sodium sulfate. The product was purified by silica gel column chromatography (CH₂Cl₂/Hexane 1/2 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 54%).

1H NMR (CDCl₃) δ 8.72 (s, 2H), 7.25 (s, 2H), 4.22 (t, 4H, J = 6.8 Hz), 1.95 (m, 4H), 1.54 (m, 4H), 1.46-1.20 (m, 24H), 0.88 (t, 6H, J = 7.0 Hz).

13C NMR (CDCl₃) δ 155.28, 142.46, 141.17, 138.84, 107.33, 105.34, 69.41, 31.92, 29.63, 29.58, 29.37, 29.36, 28.72, 26.04, 22.70, 14.12.

[M+H]⁺: Calcd 745.16; Found 745.1.

**Compound 6**

1,2-Diamino-3,6-dibromobenzene (676 mg, 2.54 mmol) was dissolved in 55 mL absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (356 mg, 2.54 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N₂ flow. The reaction mixture was cooled slightly. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 50 mL DMF, followed by addition of K₂CO₃ (1.23 g, 8.89 mmol). Then bromodecane (1.69 g, 7.62 mmol) was added and the mixture was maintained at 60 °C for 24 hrs with continuous stirring. The mixture was cooled down to room temperature and poured into 500 mL of H₂O, filtered and washed thoroughly with H₂O. It was then dried over anhydrous sodium sulfate. The product was purified by silica gel column chromatography (CH₂Cl₂/Hexane 1/3 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 56%).

1H NMR (CDCl₃) δ 7.93 (s, 2H), 7.48 (s, 2H), 4.25 (t, 4H, J = 6.6 Hz), 1.97 (m, 4H), 1.55 (m, 4H), 1.46-1.20 (m, 24H), 0.89 (t, 6H, J = 6.8 Hz).

13C NMR (CDCl₃) δ 155.64, 142.78, 139.51, 131.57, 123.20, 105.45, 69.63, 31.92, 29.60, 29.57, 29.36, 29.33, 28.73, 26.00, 22.70, 14.13.

[M+H]⁺: Calcd 651.19; Found 651.1.

2. **Drop casting film on cover glass**

Cast films of compounds 1-6 were made as follows. First, each compound (3-4 mg) was dissolved in 0.5 mL of CH₂Cl₂; the solution (ca. 0.1 mL) was drop-cast onto a clean cover glass surface. Then it was left undisturbed for several minutes, until the solvents evaporated. A raw crystalline structure of each compound was formed on top of the cover glass. The cast film experiment was carried out twice and the data are reproducible.

3. **Phase transfer (PT) self-assembly**

The solution based SA was performed using a phase transfer (PT) method in a CH₂Cl₂/methanol binary solvent system. All solvents were filtered through a 0.2 μm PTFE filter before each PT experiment. A homogeneous solution (typically 2 mL of 5 mM solution) of the compound was prepared in a “good” solvent (CH₂Cl₂) and was filtered through a 0.2 μm PTFE filter into a clean 20 mL screw-cap vial. The “poor” solvent (10 mL of methanol) was slowly
added to the CH$_2$Cl$_2$ solution so that two phases could be maintained. The binary solvent mixture was then left undisturbed overnight to induce 1-D assembly. The volume ratio of CH$_2$Cl$_2$/methanol was kept constant (1/5 v/v).

4. Gelling ability of compounds 1-6

Gels were prepared by weighing a specified amount of compound (typically 10-15 mg) and solvent (volume is dependent of the concentration specified in the Table S.1) into a 3 mL 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 1-6 at room temperature

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>PPT (5mM)</td>
<td>PPT (2mM)</td>
<td>PPT (0.7mM)</td>
<td>PPT (&lt; 0.1mM)</td>
<td>PPT (&lt; 0.1mM)</td>
<td>PPT(&lt; 0.1mM)</td>
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<tr>
<td>Ethanol</td>
<td>S</td>
<td>G (50mM)</td>
<td>PG (50mM)</td>
<td>G (43mM)</td>
<td>PG (50mM)</td>
<td>G (12mM)</td>
</tr>
<tr>
<td>Propanol</td>
<td>S</td>
<td>G (48mM)</td>
<td>G (21mM)</td>
<td>G (50mM)</td>
<td>G (42mM)</td>
<td>G (14mM)</td>
</tr>
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<td>PG (50mM)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>S</td>
<td>G (45mM)</td>
<td>G (34mM)</td>
<td>PG (50mM)</td>
<td>PG (50mM)</td>
<td>G (34mM)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>S</td>
<td>G (37mM)</td>
<td>PG (50mM)</td>
<td>G (40mM)</td>
<td>PPT (50mM)</td>
<td>G (19mM)</td>
</tr>
<tr>
<td>Hexane</td>
<td>S</td>
<td>PG (50mM)</td>
<td>PPT (50mM)</td>
<td>PPT (50mM)</td>
<td>PPT (50mM)</td>
<td>G (38mM)</td>
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<tr>
<td>TCE</td>
<td>S</td>
<td>PG (50mM)</td>
<td>S</td>
<td>S</td>
<td>PPT (50mM)</td>
<td>S</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>S</td>
<td>PG (50mM)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>TCTFE</td>
<td>S</td>
<td>PPT (50mM)</td>
<td>G (38mM)</td>
<td>PPT (50mM)</td>
<td>PPT (50mM)</td>
<td>G (35mM)</td>
</tr>
</tbody>
</table>

TCE: 1,1,1-trichloroethane, CCl$_4$: carbon tetrachloride, TCTFE: 1,1,2-trichloro-2,2,1-trifluoroethane
G: gel, PG: partial gel, ppt: precipitate, S: soluble (tested up to 50mM).
Concentration for G is critical gel concentration (CGC).

References