Bending Nanofibers into Nanospirals: Coordination Chemistry as a Tool for Shaping Hydrophobic Assemblies

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Syntheses and characterization

Scheme S1: Synthesis of the compounds 2-4, 6, 7.
**Compound 2**

**Figure S1.** $^1$H NMR spectrum of the compound 2 in CDCl$_3$.

**Figure S2.** MALDI-TOF-MS spectrum of the compound 2.
**Compound 3**

Figure S3. $^1$H NMR spectrum of the compound 3 in CDCl$_3$.

Figure S4. MALDI-TOF-MS spectrum of the compound 3.
Figure S5. $^1$H NMR spectrum of compound 4 in CDCl$_3$. 
Figure S6. MALDI-TOF-MS spectrum of the compound 4.

**Compound 6**

**Synthesis of the compound 6**: ZnBr₂ (60 μL of 0.1 M THF solution, 6·10⁻³ mmol) was added to a fluorescent red solution of 1 (9.3 mg, 5.7·10⁻³ mmol) in THF (2 mL). The solution immediately became maroon. It was kept with stirring for one hour at ambient temperature. The volatiles were evaporated, the residue was thoroughly washed with Et₂O (10 mL); then dissolved in chloroform to give a maroon fluorescent solution, filtered through a cotton pad and dried under vacuum to give 10.6 mg (100%) of the product as a maroon solid.

¹H NMR (300 MHz, CDCl₃, 20°C): δ = 10.08 (d, ³J (H,H) = 8.2 Hz, 1 H; perylene), 9.74 (d, ³J (H,H) = 8.5 Hz, 1 H; perylene), 9.22 (d, ³J (H,H) = 4.2 Hz, 2 H; terpy-H6), 8.94 (s, 1 H; perylene), 8.70 (d, ³J (H,H) = 8.5 Hz, 1 H; perylene), 8.68 (d, ³J (H,H) = 8.5 Hz, 1 H; perylene), 8.52 (s, 1 H; perylene), 8.45 (s, 2 H; terpy-H³'), 8.32 (d, ³J (H,H) = 8.0 Hz, 2 H; terpy-H3), 8.09 (t, ³J (H,H) = 7.8 Hz, 2 H; terpy-H4), 7.94 (d, ³J (H,H) = 8.3 Hz, 2 H; phenyl), 7.84 (d, ³J (H,H) = 8.4 Hz, 2 H; phenyl), 7.72 (dd, ³J (H,H) = 7.0 Hz, ³J (H,H) = 5.3 Hz, 2 H; terpy-H5), 5.10 (m, 2 H; CH, ethylpropyl), 4.69 (m, 2 H; CH₂, PEG), 4.12 (m, 2 H; CH₂, PEG), 3.87 (m, 2 H; CH₂, PEG), 3.80 (m, 2 H; CH₂, PEG), 3.73-3.53 (m, 62 H; CH₂, PEG), 3.37 (s, 3 H; CH₃, PEG), 2.30 (m, 4 H; CH₂, ethylpropyl), 1.96 (m, 4 H; CH₂, ethylpropyl), 0.95 ppm (t, ³J (H,H) = 7.4 Hz, 12 H; CH₃, ethylpropyl); confirmed by COSY and NOE.
MALDI-TOF-MS (DCTB matrix) m/z calc. for [M – Br], C_{90}H_{109}BrN_{5}ZnO_{21}: 1738.61; found: 1739.18 (Figure S9).

**Figure S7.** Normalized UV/Vis spectra of a solution of 6 in chloroform (solid line) and in water/THF (19:1 v/v) solution after 2 days aging (dashed line); normalized fluorescence spectrum of a solution of 6 in chloroform (grey line).

**Figure S8.** ^1^H NMR spectrum of compound 6 in CDCl₃.
Figure S9. MALDI-TOF-MS spectrum of the compound 6.

Figure S10. Cryo-TEM images of a solution of 6 (1·10⁻⁴ M) in water/THF (19/1 v/v) after: a) 2 days and b) 21 days of aging (scale bar: 50 nm in the images A-B; 20 nm in the inset of the image B).

**Compound 7**

**Synthesis of the compound 7:** ZnI₂ (40 μL of 0.1 M THF solution, 4·10⁻³ mmol) was added to a fluorescent red solution of 1 (6.2 mg, 3.8·10⁻³ mmol) in THF (2 mL). The solution immediately became maroon. It was kept with stirring for one hour at ambient temperature. The volatiles were evaporated and the residue was thoroughly washed with Et₂O (10 mL); then dissolved in chloroform to give a maroon fluorescent solution,
filtered through a cotton pad and dried under vacuum to give 6.8 mg (91.6%) of the product as a purple solid.

$^1$H NMR (300 MHz, CDCl$_3$, 20°C): $\delta = 10.08$ (d, $^3J$ (H,H) = 8.26 Hz, 1 H; perylene), 9.74 (d, $^3J$ (H,H) = 8.43 Hz, 1 H; perylene), 9.26 (d, $^3J$ (H,H) = 4.04 Hz, 2 H; terpy-H6), 8.94 (s, 1 H; perylene), 8.70 (d, $^3J$ (H,H) = 7.94 Hz, 1 H; perylene), 8.68 (d, $^3J$ (H,H) = 7.23 Hz, 1 H; perylene), 8.52 (s, 1 H; perylene), 8.47 (s, 2 H; terpy-H3’), 8.32 (d, $^3J$ (H,H) = 8.02 Hz, 2 H; terpy-H3), 8.10 (td, $^3J$ (H,H) = 7.77 Hz, $^4J$ (H,H) = 1.51 Hz, 2 H; terpy-H4), 7.94 (d, $^3J$ (H,H) = 8.24 Hz, 2 H; phenyl), 7.86 (d, $^3J$ (H,H) = 8.34 Hz, 2 H; phenyl), 7.74 (dd, $^3J$ (H,H) = 7.1 Hz, $^3J$ (H,H) = 5.2 Hz, 2 H; terpy-H5), 5.10 (m, 2 H; CH, ethylpropyl), 4.69 (m, 2 H; CH$_2$, PEG), 4.12 (m, 2 H; CH$_2$, PEG), 3.87 (m, 2 H; CH$_2$, PEG), 3.80 (m, 2 H; CH$_2$, PEG), 3.73-3.53 (m, 64 H; CH$_2$, PEG), 3.37 (s, 3 H; CH$_3$, PEG), 2.30 (m, 4 H; CH$_2$, ethylpropyl), 1.96 (m, 4 H; CH$_2$, ethylpropyl), 0.95 ppm (t, $^3J$ (H,H) = 7.42 Hz, 12 H; CH$_3$, ethylpropyl)

MALDI-TOF-MS (DCTB matrix) m/z calc. for [M – I], C$_{90}$H$_{109}$ln$_5$ZnO$_{21}$: 1786.60; found: 1787.20 (Figure S13).

**Figure S11.** Normalized UV/Vis spectra of a solution of 7 in chloroform (solid line) and in water/THF (19:1 v/v) solution after 2 days aging (dashed line); normalized fluorescence spectrum of a solution of 7 in chloroform (grey line).
Figure S12. $^1$H NMR spectrum of compound 7 in CDCl$_3$.

Figure S13. MALDI-TOF-MS spectrum of the compound 7.
Figure S14. Cryo-TEM images of a solution of 7 (1·10^{-4} M) in water/THF (19/1 v/v) after: a) 2 days and b) 21 days of aging (scale bar: 50 nm in all images).

Table S1:

<table>
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<th>Cmpd.</th>
<th>Absorption(^a) (\lambda_{abs} (\text{nm}) (\epsilon (\text{M}^{-1} \text{cm}^{-1})))</th>
<th>Fluorescence(^a) (\lambda_{max} (\text{nm}))</th>
<th>Q. Y.(^b)</th>
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<tbody>
<tr>
<td>6</td>
<td>577 (27400), 538 (20400), 384 (25700)</td>
<td>603</td>
<td>0.54</td>
</tr>
<tr>
<td>7</td>
<td>577 (31200), 539 (23400), 385 (30200)</td>
<td>602</td>
<td>0.58</td>
</tr>
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</table>

\(^a\) In CH\(_2\)Cl\(_2\); \(^b\) determined using Sulforhodamine 101 solution in ethanol as a standard

Table S2: Zeta potentials, \(\zeta\) (mV), of solutions of 6 and 7 (1·10^{-4} M) in water/THF (19/1 v/v) measured after specified period of aging.

<table>
<thead>
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<th>Aging</th>
<th>Complex</th>
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<tr>
<td>2 days</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>23.8±6.31</td>
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</table>

Reaction of 2 with KCN at 0 aging in self-assembling environment.

Complex 2 (2·10^{-4} mmol) was dissolved in THF (110 \(\mu\)L). Sonication (5-10 min) was required to achieve complete dissolving. The resulting THF solution was quickly added to aqueous solution containing 2 eq. of KCN (1.9 ml; 2.1·10^{-4} M KCN) and vigorously mixed. A purple precipitate appeared after a few minutes.
Figure S15. Cryo-TEM images of a solution of 2 (1·10⁻⁴ M) in KCN/water/THF (2·10⁻⁴ M, 19:1 v/v) after 2 days of aging (scale bar: 100 nm).

Cryo-TEM images showed formation of crystallites consisting of interacting straight fibers 2.0±0.3 nm in width. The periodicity of the crystalline aggregates varied due to different angle towards the focal plane. The spacing for the crystallites that are oriented parallel to the focal plane is ca. 3.5 nm. Linear rigid geometry of the fibers can be explained by cyanide coordination, which prevented formation of bridging bonds between adjacent zinc(II) atoms. No formation of spirals or toroids was observed.
**Figure S16.** UV/Vis spectra of a solution of 2 (1·10⁻⁴ M) in water/THF (19:1 v/v) solution after 6 minutes (black solid line) and 2 days (black dashed line) aging; UV/Vis spectra of a solution of 2 (1·10⁻⁴ M) in KCN/water/THF (2·10⁻⁴ M, 19:1 v/v) solution after 7 minutes (grey solid line) and 2 days (grey dashed line) aging.