

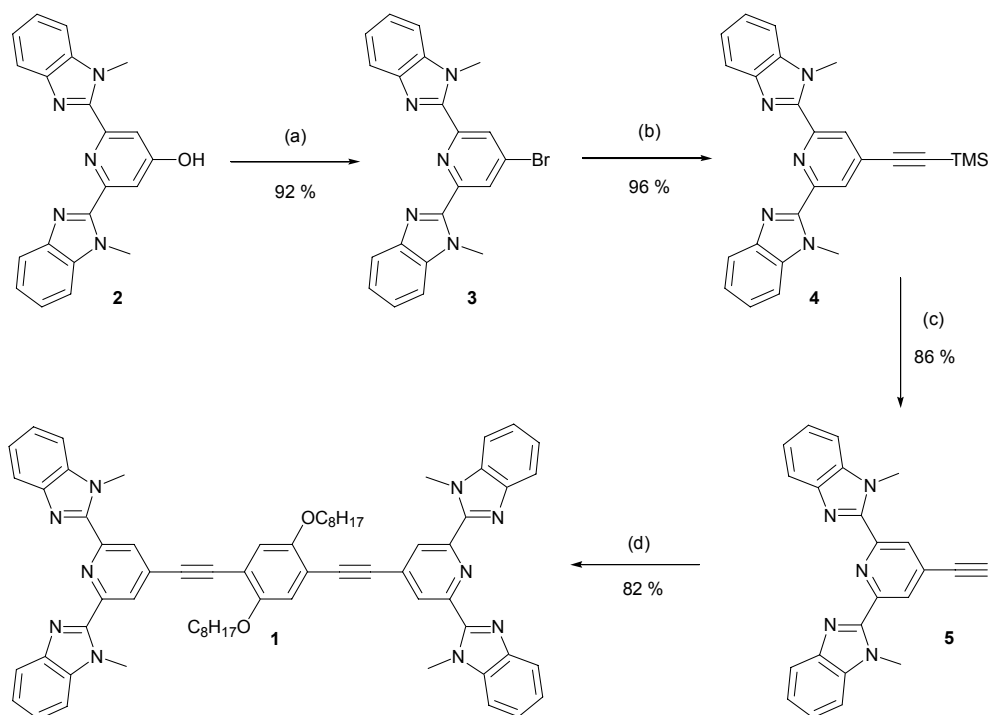
Supplementary Material (ESI) for Chemical Communications
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Synthesis and optical properties of metallo-supramolecular polymers

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Electronic Supplementary Material



(a) POBr_3 , 140 °C. (b) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , Et_3N , DMF , Me_3SiCCH , 55 °C. (c) KOH , THF/MeOH , RT. (d) $\text{Pd}(\text{PPh}_3)_4$, CuI , Diisopropylamine, 1,4-diiodo-2,5-dioctyloxyphenyl, 75 °C.

Scheme 1: Synthesis of ditopic monomer **1**.

Methods: All chemicals were of highest commercial quality and were used as received, unless otherwise noted. ¹H NMR spectral data are expressed in ppm relative to internal TMS and were obtained on a Varian Gemini 300 MHz NMR spectrometer. All electronic spectra were measured in CH₃CN/CHCl₃ (1/9 v/v), which is a suitable solvent for all compounds studied here. UV-Vis absorption spectra were obtained on a Perkin Elmer Lambda 800. PL spectra were measured on a PTI C720 fluorescence spectrometer. Mass spectroscopy was carried out on a Bruker Biflex III spectrometer.

Synthesis of 2,6-bis(1'-methyl-benzimidazolyl)-4-bromopyridine (3).

2,6-Bis(1'-methyl-benzimidazolyl)-4-hydroxypyridine (**2**) (1.0 g, 2.81 mmol) was added to a round bottom flask attached with a reflux condenser. A large excess of phosphorous oxybromide was added to the flask and the reaction was heated at 140 °C for 16 hours under a nitrogen atmosphere. The homogenous solution was then poured hot into water and the pH was adjusted to 8.0 by addition of 10 % NaOH solution. The reaction flask was rinsed with dichloromethane which was subsequently added to the stirred aqueous solution. The mixture was stirred for an hour and the organic layer was separated off. The aqueous layer was extracted with dichloromethane twice and the combined organic layers were washed once with water, dried with anhydrous sodium sulfate before being filtered. The solvent was evaporated yield **3** as a yellow brown solid. (1.08 gm 92 %). ¹H NMR (300 MHz, DMSO): δ 8.55(s, 2H), 7.78-7.69(m, 4H), 7.39-7.32(m, 4H), 4.25(s, 6H). ¹³C NMR (75 MHz, DMSO): δ 150.54, 148.46, 142.00, 137.20, 133.50, 127.29, 123.75, 122.81, 119.70, 111.12, 32.66. (MS-MALDI-HABA) 419.21

Synthesis of 2,6-bis(1'-methyl-benzimidazolyl)-4-trimethylsilylethynylpyridine (4).

3 (1.0 g, 2.39 mmol), Pd(PPh₃)₂Cl₂ (0.0838 g, 0.119 mmol), CuI (0.022 g, 0.119 mmol), triethylamine (14 mL) and dimethylformamide (11 mL) were added to a flask with a reflux condenser and were purged with nitrogen for 30 minutes. The reaction mixture was heated to 55 °C and trimethylsilylacetylene (0.85 mL, 5.98 mmol) was added. Stirring was continued for an hour and the hot reaction mixture was poured in to a saturated aqueous EDTA solution (100 mL) and chloroform (20mL) was added. After stirring for a further hour the organic layer was separated and the aqueous layer extracted with chloroform. The combined organic layers were washed once with water and dried with anhydrous sodium sulfate before being filtered. The solvent was evaporated to give a brown solid. Purification was carried out by chromatography using a silica gel column with chloroform as the eluent, to yield **4** as a white yellow solid (1.005 g, 96.3 %). ¹H NMR (300 MHz, CDCl₃): δ 8.425 (s, 2H), 7.83-7.80 (m, 4H), 7.35-7.29 (m, 4H), 4.14(s, 6H), 0.28 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 149.62, 149.43, 142.46, 137.08, 133.47, 127.03, 123.69, 122.87, 120.10, 109.89, 101.79, 101.14, 32.44, -0.38. MS (MALDI-HABA) 437.34, 459.12 (Na+).

Synthesis of 2,6-bis(1'-methyl-benzimidazolyl)-4-ethynylpyridine (5).

4 (0.750g, 1.71 mmol), aqueous NaOH (25 ml, 20 %), tetrahydrofuran (25 ml, freshly distilled) and methanol (25 ml) were stirred at room temperature for 4 hours. The organic layer was separated and the aqueous layer extracted with chloroform. The combined organic layers were washed once with water and dried with anhydrous sodium sulfate before being filtered. The solvent was evaporated to give brown solid. Purification was

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carried out by chromatography using a silica gel column with chloroform as the eluent, to yield **5** as a white solid (0.542 g, 86.8 %). ¹H NMR (300 MHz, CDCl₃): δ 8.48 (s, 2H), 7.87-7.85 (m, 4H), 7.46-7.34 (m, 4H), 4.22(s, 6H), 3.41 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 149.98, 149.60, 142.69, 137.30, 132.91, 127.56, 123.96, 123.12, 120.43, 110.09, 83.44, 80.26 32.63. MS (MALDI-HABA) 363.91, 385.90 (Na⁺), 401.83(K⁺).

Synthesis of Ditopic Monomer **1**

5 (0.190 g, 0.522 mmol), 1,4-diiodo-2,5-dioctyloxybenzene (0.149 g, 0.255 mmol), Pd(PPh₃)₄ (0.0176 g, 0.0153mmol), CuI (0.0029 g, 0.0153 mmol), toluene (8 mL) and diisopropylamine (3 mL) were added to a flask with a reflux condenser and the mixture was stirred at 70 °C for 22 hrs under nitrogen. The hot reaction mixture was subsequently poured into saturated aqueous EDTA solution (100 mL) and chloroform (20mL) was added. After stirring for a further hour the organic layer was separated and the aqueous layer extracted with chloroform. The combined organic layers were washed once with water and dried with anhydrous sodium sulfate before being filtered. The solvent was evaporated to give an orange solid. Purification was carried out by chromatography using a silica gel column with 0.5 % methanol in dichloromethane as the eluent, to yield **1** as a yellow solid (0.220 g, 82 %). ¹H NMR (300 MHz, CDCl₃): δ 8.55 (s, 4H), 7.91-7.88 (m, 4H), 7.49-7.35 (m, 12H), 7.09 (s, 2H), 4.27 (s, 12H), 4.12-4.08 (t, 4H), 1.95-1.90 (m, 4H), 1.59-1.21 (m, 20H), 0.81-0.77 (t, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 154, 150, 149.97, 142.84, 137.40, 134.24, 127.04, 123.92, 123.12, 120.51, 117.64, 114.01, 110.10, 92.52, 91.90, 69.94, 32.68, 31.97, 29.52, 29.46, 29.35, 26.21, 22.78, 14.19. MS (MALDI-α-cyano) 1058.05.

UV and PL titration experiments of **1** with Zinc perchlorate hexahydrate

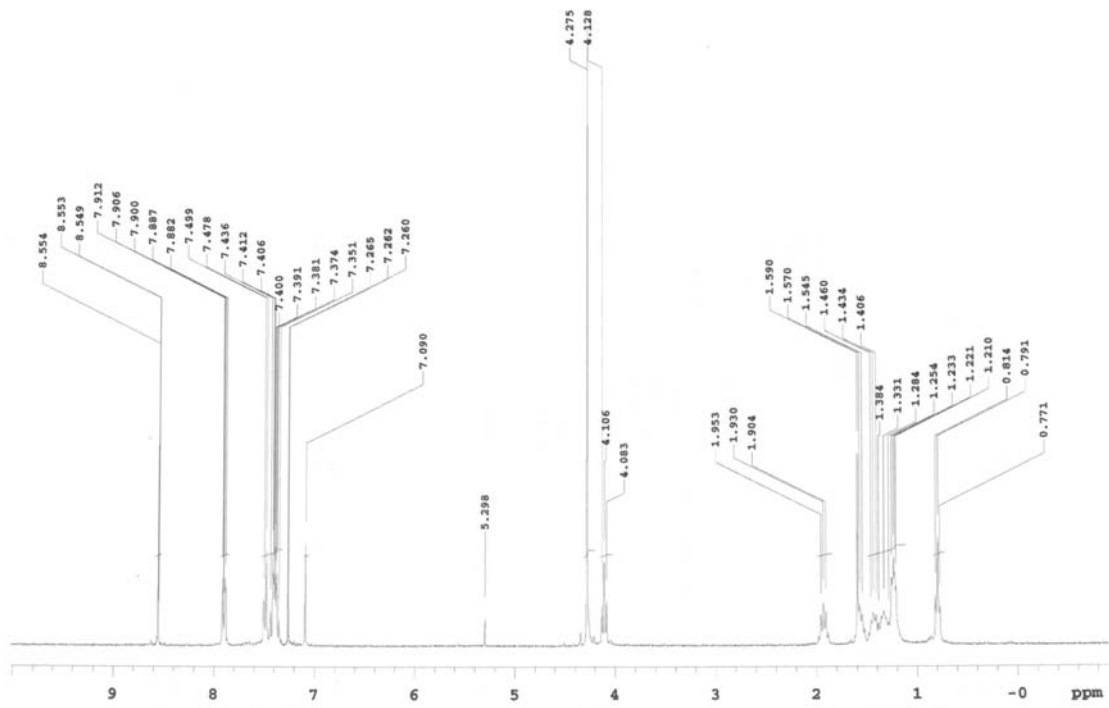
A 1.0·10⁻⁵ M solution of **1** in a mixture of CH₃CN/CHCl₃ (1/9 v/v) was titrated with 66 μl aliquots of a solution of the same solvent composition, which is 13.4·10⁻⁵ M in Zn(ClO₄)₂ and 1.0·10⁻⁵ M in **1**. The addition was done stepwise and the formation of Zn(II)-coordination polymers was monitored by UV-vis or photoluminescence spectroscopy.

Viscosity measurements

Viscosity measurements were done at 25 °C with a micro-Ubbelohde viscometer using separate dimethyl acetamide (DMAc) solutions that comprised **1** and Zn(ClO₄)₂ in different molar ratios. The total solute concentration was kept always constant at 35 mg/mL.

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^1H NMR of **1** (300 MHz, CDCl_3)



^{13}C NMR of **1** (75 MHz, CDCl_3)

