Electronic Supplementary Information for

Self-assembly and layer-by-layer deposition of

metallosupramolecular perylene bisimide polymers

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Material and methods

Solvents were purified and dried according to standard procedures. Column chromatography was performed with silica gel (0.035-0.070 mm) and basic alumina, the latter was deactivated with 4 weight % of water to activity II. Zinc trifluoromethane sulfonate salt was obtained from commercial sources. MALDI-TOF mass spectra were measured using a Bruker Autoflex II spectrometer in reflector mode. $^1$H NMR spectra were recorded at 298 K on a Bruker Avance 400 spectrometer (400 MHz) and chemical shifts $\delta$ (ppm) were calibrated against tetramethylsilane (Me$_4$Si) as internal reference. $^1$H DOSY experiments were carried out at 298 K on a Bruker DMX 600 spectrometer (600 MHz) equipped with a BGPA 10 gradient generator, a BGU II control unit, and a conventional 5 mm broadband ($^{15}$N-$^{31}$P)/$^1$H probe with automatic tune/match accessory and $z$ axis gradient coil capable of producing pulsed magnetic field gradients in the $z$ direction of 52 G cm$^{-1}$. For the measurement of UV-vis spectra, PerkinElmer Lambda 950 spectrometer was used. The steady-state fluorescence spectra were measured on a PTI QM-4/2003 spectrometer and fluorescence quantum yields were determined by optical dilute method (A < 0.05) using $N,N'$-di(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxypyrene-3,4:9,10-tetracarboxylic acid bisimide ($\Phi_I = 0.96$ in chloroform) and Nileblue a ($\Phi_I = 0.27$ in ethanol) as standards. The solvents for spectroscopic studies were of spectroscopic grade and used as received. Fluorescence lifetimes were determined with a fluorescence lifetime measurement system by using a PTI GL330 nitrogen laser (337 nm) and a PTI GL302 dye laser. Fluorescence decay curves were evaluated by using the software supplied with the instrument. AFM measurements were carried out under ambient conditions by using a Veeco MultiMode™ Nanoscope IV system operating in tapping mode in air.
Synthesis of perylene bisimide building blocks

$N,N'$-Bis(4'-2,2':6',2''-terpyridyl)-1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic acid bisimide (3)

A mixture of 50.0 mg (0.094 mmol) of 1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic acid bisanhydride $^5$ (1) and 70.3 mg (0.28 mmol) of 4'-amino-2,2':6',2''-terpyridine $^6$ was heated in pyridine/imidazole (2:1) under stirring at 120 °C for 48 h under argon. After cooling to room temperature, the mixture was poured into aqueous HCl (10 mL, 1 M). The resulting precipitate was separated by filtration, washed with water (6 × 50 mL) and purified by column chromatography with dichloromethane/acetone (97:3) to yield 55 mg (59%) of 3 as a dark-green powder.

$\text{Mp} > 350 \degree \text{C;} \quad m/z \ (\text{FAB}) = 991.59 \ [\text{M}^+] , \ 992.60 \ [\text{M}^+\text{H}] \ \text{calc. for C}_{62}\text{H}_{42}\text{N}_{10}\text{O}_4 \ 991.06 ; \ m/z \ (\text{HRMS, ESI, pos.}) = 990.3385 \ [\text{M}^+] \ \text{calc. for C}_{62}\text{H}_{42}\text{N}_{10}\text{O}_4 \ 990.3390 ; \ \delta_t \ (400 \text{MHz, CDCl}_3, \text{Me}_4\text{Si}) : \ 8.71 \ (d, \ J = 6.9 \ \text{Hz}, \ 4\text{H, H6,6''}), \ 8.68 \ (d, \ J = 5.6 \ \text{Hz}, \ 4\text{H, H3,3''}), \ 8.57 \ (s, \ 2\text{H, Hpery}), \ 8.55 \ (s, \ 4\text{H, H3',5'}), \ 8.53 \ (d, \ J = 8.0 \ \text{Hz}, \ 2\text{H, Hpery}), \ 7.87-7.91 \ (m, \ 4\text{H, H4,4''}), \ 7.80 \ (d, \ J = 8.0 \ \text{Hz}, \ 2\text{H, Hpery}), \ 7.32-7.35 \ (m, \ 4\text{H, H5,5''}), \ 3.72-3.91 \ (m, \ 4\text{H, HPyrrolidinyl}), \ 2.87-3.02 \ (m, \ 4\text{H, HPyrrolidinyl}), \ 1.97-2.18 \ (m, \ 8\text{H, HPyrrolidinyl}); \ \lambda_{\text{max}} \ (\text{CH}_2\text{Cl}_2)/\text{nm} = 714 \ (\epsilon/\text{M}^\text{1}\cdot\text{cm}^\text{-1} \ 48200), \ 437 \ (18900), \ 279 \ (67000), \ 250 \ (89200); \ \text{fluorescence} \ \lambda_{\text{max}} \ (\text{CH}_2\text{Cl}_2, \ \lambda_{\text{ex}} = 660 \ \text{nm})/\text{nm} = 750, \ \text{quantum yield} \ \Phi_{\text{f1}} \ (\text{CH}_2\text{Cl}_2) = 0.26\pm0.01; \ \text{fluorescence lifetime} \ \tau \ (\text{CH}_2\text{Cl}_2, \ \lambda_{\text{ex}} = 660 \ \text{nm}, \ \lambda_{\text{em}} = 745 \ \text{nm})/\text{ns} = 3.8\pm0.2.$

$N,N'$-Bis(4'-2,2':6',2''-terpyridyl)-1,6,7,12-tetra(4-tert-octylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide (4a)

1,6,7,12-Tetra(4-tert-octylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisanhydride $^7$ (2a) (0.13 mg, 0.11 mmol) was reacted with 4'-amino-2,2':6',2''-terpyridine (0.79 g, 0.32 mmol) in pyridine/imidazole (2:1) for 24 h at 120 °C under argon. After cooling to room temperature, the mixture was poured into aqueous HCl (70 mL, 1 M); the resulting precipitate was isolated by filtration and subsequently washed
with water (20 mL) and methanol (20 mL). Purification was achieved by column chromatography on aluminium oxide (basic, activity II) with CH₂Cl₂/n-hexane (80:20) to yield 4a (83 mg, 46%) as a dark-red microcrystalline powder.

Mp > 350 °C; m/z (FAB) = 1670.3 [M⁺], 1671.3 [M⁺+H], calc. for C₁₁₀H₁₀₈N₈O₈ 1670.08; δt (400 MHz, CDCl₃, Me₄Si): 8.65 (d, J = 6.9 Hz, 4H, H6,6''), 8.64 (d, J = 4.8 Hz, 4H, H3,3''), 8.45 (s, 4H, H3',5''), 8.21 (s, 4H, Hpery), 7.81-7.86 (m, 4H, H4,4''), 7.25-7.31 (m, 12H, H₅,5''), 6.91 (d, J = 8.7 Hz, 8H, H₆r), 1.70-2.18 (s, 12H, CH₂), 1.33 (s, 24H, CH₃), 0.74 (s, 36H, CH₃); λmax (CH₂Cl₂)/nm = 588 (ε/M⁻¹cm⁻¹ 50800), 550 (30300), 456 (17200), 239 (106800); fluorescence λmax (CH₂Cl₂, λex = 540 nm)/nm = 618, quantum yield Φ₁(CH₂Cl₂) = 0.96±0.01; fluorescence lifetime τ (CH₂Cl₂, λex = 540 nm, λem = 617 nm)/ns = 6.6±0.2; found: C 78.73, H 6.81, N 6.55; calc. for C₁₁₀H₁₀₈N₈O₈ (1670.3): C 79.11, H 6.52, N 6.71.

N,N'-Bis(4'-2,2':6',2''-terpyridyl)-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide (4b)

This compound was synthesized and purified according to procedure as described for 4a from 1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisanhydride (2b) (0.15 g, 0.15 mmol) and 4'-amino-2,2':6',2''-terpyridine (0.15 g, 0.61 mmol), to give 4b (0.11 g, 50%) as a bright-red powder.

Mp > 350 °C; m/z (FAB) = 1445.5 [M⁺], calc. for C₉₄H₇₆N₈O₈ 1445.6; m/z (HRMS, ESI, pos.) = 1445.5859 [M⁺], calc. for C₉₄H₇₆N₈O₈ 1445.5820; δt (400 MHz, CDCl₃, Me₄Si): 8.65 (d, J = 6.9 Hz, 4H, H6,6''), 8.64 (d, J = 4.8 Hz, 4H, H3,3''), 8.46 (s, 4H, H3',5''), 8.28 (s, 4H, Hpery), 7.82-7.88 (m, 4H, H₄,4''), 7.29-7.33 (m, 4H, H₅,5''), 7.24 (d, 8H, J = 8.7 Hz, H₆r), 6.88 (d, J = 8.7 Hz, 8H, H₆r), 1.26 (s, 36H, CH₃); λmax (CH₂Cl₂)/nm = 585 (ε/M⁻¹cm⁻¹ 54200), 544 (32500), 456 (18400), 281 (89400); fluorescence λmax (CH₂Cl₂, λex = 540 nm)/nm = 615, quantum yield Φ₁(CH₂Cl₂) = 0.97±0.01.

N-Cyclohexyl-N'-(4'-2,2':6',2''-terpyridyl)-1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic
acid bisimide (7)

N-Cyclohexyl-1,7-dipyrroloidinylpyrene-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide (7) (150 mg, 0.25 mmol) was reacted with 4′-amino-2,2′:6′,2″-terpyridine (91.3 g, 0.37 mmol) in pyridine/imidazole (2:1) for 50 h at 120 °C under argon. After cooling to room temperature, the mixture was poured into aqueous HCl (20 mL, 1 M); the resulting precipitate was extracted with 90 mL of methylene chloride, washed with water, dried over MgSO₄, and concentrated by rotary evaporation. Purification was achieved by column chromatography on silica gel with CH₂Cl₂/methanol (99:1) to yield 7 (140 mg, 68%) as a dark-green microcrystalline powder.

Mp > 330 °C; m/z (MALDI-TOF, dithranol) = 841.18 [M⁺], 842.18 [M⁺+H] calc. for C₅₃H₄₃N₇O₄ 841.95; δ₁ (400 MHz, CDCl₃, Me₄Si): 8.70 (d, J = 7.9 Hz, 2H, H₆,6''), 8.67 (d, J = 4.4 Hz, 2H, H₃,3''), 8.54 (s, 1H, H₇pery), 8.54 (s, 2H, H₃',5''), 8.51 (s, 1H, H₇pery), 8.49 (d, J = 9.4 Hz, 1H, H₇pery), 8.44 (d, J = 8.1 Hz, 1H, H₇pery), 7.85-7.89 (m, 2H, H₄,4''), 7.80 (d, J = 8.0 Hz, 1H, H₇pery), 7.75 (d, J = 8.0 Hz, 1H, H₇pery), 7.32-7.35 (m, 2H, H₅,5''), 5.00-5.14 (m, 1H, NCH₂), 3.70-3.90 (m, 4H, Hpyrrolidinyl), 2.80-3.00 (m, 4H, Hpyrrolidinyl), 2.56-2.67 (m, 2H, HCy), 1.89-2.10 (m, 10H, Hpyrrolidinyl, Hcy), 1.33-1.50 (m, 4H, Hcy); δ₁² (100 MHz, CDCl₃): 164.6, 164.5, 163.6, 163.5, 157.1, 155.7, 149.1, 146.8, 146.4, 145.9, 136.8, 135.1, 134.0, 130.3, 130.0, 127.3, 126.6, 124.2, 123.9, 123.8, 122.8, 122.7, 122.3, 121.6, 121.4, 121.3, 121.2, 120.8, 119.9, 118.9, 118.7, 117.7 53.8, 52.3, 29.2, 26.7, 25.8, 25.6; λₘₐₓ(CH₂Cl₂)/nm = 706 (ε/M⁻¹cm⁻¹ 41800), 436 (16600), 309 (36500), 278 (44300), 246 (69500); fluorescence λₘₐₓ(CH₂Cl₂, λₑₓ = 660 nm)/nm = 746, quantum yield Φₘ (CH₂Cl₂) = 0.19; fluorescence lifetime τ (CH₂Cl₂, λₑₓ = 660 nm, λₑₘ = 745 nm)/ns = 3.7±0.2; found: C 73.86, H 5.36, N 11.42; calc. for C₅₃H₄₃N₇O₄×H₂O (859.9): C 73.95, H 5.01, N 11.30.
**N-Butyl-N’-(4’-2,2’:6’,2’’-terpyridyl)-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide (8)**

N-Butyl-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide\(^7\) (6) (0.14 mg, 0.13 mmol) was reacted with 4’-amino-2,2’:6’,2’’-terpyridine (0.50 g, 0.20 mmol) in pyridine/imidazole (2:1) for 48 h at 120 °C under argon. After cooling to room temperature, the mixture was poured into aqueous HCl (20 mL, 1 M); the resulting precipitate was isolated by filtration and subsequently washed with water (30 mL) and methanol (20 mL). Purification was achieved by column chromatography on aluminium oxide (basic, activity II) with CH\(_2\)Cl\(_2\)/n-hexane (80:20) to yield 6 (84 mg, 50%) as a dark-red microcrystalline powder.

Mp > 320 °C; \(m/z\) (ESI, pos.) = 1270.56 [M\(^+\)], calc. for C\(_{83}\)H\(_{75}\)N\(_5\)O\(_8\) 1270.55; \(\delta\)\(_1\) (400 MHz, CDCl\(_3\), Me\(_4\)Si): 8.58 (m, 4H, H\(_6\),H\(_6\)'', H\(_3\),H\(_3\)''), 8.39 (s, 1H, H\(_3\)',H\(_5\)'), 8.18 (s, 2H, H\(_{pery}\)), 8.17 (s, 2H, H\(_{pery}\)), 7.79 (m, 2H, H\(_{4,4''}\)), 7.25 (m, 2H, H\(_{5,5''}\)), 7.17 (m, 8H, H\(_{Ar}\)), 6.78 (m, 8H, H\(_{Ar}\)), 4.05 (m, 2H, NCH\(_2\)), 1.61 (m, 2H, CH\(_2\)), 1.34 (m, 2H, CH\(_2\)), 1.22 (s, 18H, CH\(_3\)), 1.18 (s, 18H, CH\(_3\)); \(\lambda_{\text{max}}\) (CH\(_2\)Cl\(_2\))/nm = 581 (\(\varepsilon/M^1 cm^{-1}\) 46100), 541 (27800), 453 (16600), 285 (64000); fluorescence \(\lambda_{\text{max}}\) (CH\(_2\)Cl\(_2\), \(\lambda_{\text{ex}} = 540\ nm\))/nm = 611, quantum yield \(\Phi_h\) (CH\(_2\)Cl\(_2\)) = 0.89±0.01; fluorescence lifetime \(\tau\) (CH\(_2\)Cl\(_2\), \(\lambda_{\text{ex}} = 540\ nm\), \(\lambda_{\text{em}} = 617\ nm\))/ns = 7.2±0.2; found: C 78.18, H 5.86, N 5.42; calc. for C\(_{83}\)H\(_{75}\)N\(_5\)O\(_8\) (1270.56): C 78.46, H 5.95, N 5.51.
Metal-ion-mediated self-assembly of perylene bisimide building blocks

Metallo-dimer (7)$_2$Zn(OTf)$_2$

To a solution of $N$-cyclohexyl-$N'$-(4'-2,2':6',2''-terpyridyl)-1,7-dipyrrolidinylperylen-3,4:9,10-tetracarboxylic acid bisimide 7 (10.0 mg, 11.8 µmol) in CHCl$_3$/CH$_3$OH (60:40, 0.65 mL) a stock solution of zinc triflate (16.8 mM, 350 µL, 5.9 µmol) was added and the solution was stirred for 10 min at room temperature. The solution was concentrated by rotary evaporation; the product was precipitated by addition of acetonitrile (10 mL) and isolated quantitatively by centrifugation. Exact 2:1 stoichiometry of 7 and zinc triflate was confirmed by $^1$H NMR.

$m/z$ (MALDI-TOF, dithranol) = 1895.50 [M-OTf]$^+$, 1746.50 [M-2OTf]$^+$, 1054.20 [7+Zn+OTf]$^+$ calc. for C$_{108}$H$_{86}$F$_6$N$_{14}$O$_{14}$S$_2$Zn 2045.51; $\delta$$_{H}$ (400 MHz, CDCl$_3$/CD$_3$OD 60:40, Me$_4$Si): 9.11 (bs, 4H, H$_{3'},5'$), 8.76 (d, $J$ = 8.1 Hz, 4H, H$_{3''}$), 8.58 (bs, 4H, H$_{pery}$), 8.42-8.49 (m, 4H, H$_{pery}$), 8.25-8.35 (m, 4H, H$_{4',4''}$), 8.07 (d, $J$ = 4.7 Hz, 4H, H$_{6',6''}$), 7.75-7.85 (m, 2H, H$_{pery}$), 7.61-7.67 (m, 4H, H$_{5',5''}$), 7.53-7.61 (m, 2H, H$_{pery}$), 5.08-5.15 (m, 2H, NCH$_2$), 3.68-3.87 (m, 8H, H$_{Pyrrolidinyl}$), 2.73-2.92 (m, 8H, H$_{Pyrrolidinyl}$), 2.61-2.72 (m, 4H, H$_{Cy}$), 1.77-2.16 (m, 28H, H$_{Pyrrolidinyl}$, H$_{Cy}$), 1.38-1.56 (m, 4H, H$_{Cy}$); $\lambda_{max}$ (CHCl$_3$/MeOH 60:40)/nm = 723 (ε/M$^{-1}$cm$^{-1}$ 78400), 441 (32000), 320 (66800), 285 (90200); fluorescence $\lambda_{max}$ (DMF, $\lambda_{ex}$ = 660 nm)/nm = 764, quantum yield $\Phi_h$ (DMF) = 0.10±0.01; fluorescence lifetime $\tau$ (CHCl$_3$/MeOH 60:40), $\lambda_{ex}$ = 660 nm, $\lambda_{em}$ = 770 nm)/ns = 1.8±0.2.

Metallo-dimer (8)$_2$Zn(OTf)$_2$

To a solution of $N$-butyl-$N'$-(4'-2,2':6',2''-terpyridyl)-1,6,7,12-tetra(4-t-butylphenoxy)perylen-3,4:9,10-tetracarboxylic acid bisimide 8 (4.94 mg, 3.88 µmol) in CHCl$_3$/CH$_3$OH (60:40, 0.70 mL) a stock solution of zinc triflate (4.85 mM, 400 µL, 1.94 µmol) was added and the solution was stirred for 10 min at room temperature. The solution was concentrated by rotary evaporation; the product was precipitated by addition of acetonitrile (10 mL) and isolated quantitatively by centrifugation. Exact 2:1
stoichiometry of ligand 8 and Zn(II) triflate was confirmed by $^1$H NMR.

$m/z$ (MALDI-TOF, DCTB) = 2754.0 [M-OTf]$^+$, 2605.0 [M-2OTf]$^+$ calc. for C$_{168}$H$_{150}$F$_6$N$_{10}$O$_{22}$S$_2$Zn 2904.5; $\delta_H$ (400 MHz, CDCl$_3$/CD$_3$OD 60:40, Me$_4$Si): 8.92 (s, 4H, H3',5''), 8.59 (d, $J$ = 8.1 Hz, 4H, H3,3''), 8.37 (s, 4H, H$_{pery}$), 8.26 (s, 4H, H$_{pery}$), 8.16-8.22 (m, 4H, H4,4''), 7.87 (d, $J$ = 5.6 Hz, 4H, H6,6''), 7.47-7.54 (m, 4H, H5,5''), 7.27-7.33 (m, 16H, H$_{Ar}$), 6.90-6.95 (m, 16H, H$_{Ar}$), 4.11-4.17 (m, 4H, NCH$_2$), 1.66-1.72 (m, 4H, CH$_2$), 1.38-1.46 (m, 4H, CH$_2$), 1.32 (s, 36H, CH$_3$), 1.29 (s, 36H, CH$_3$), 0.93-0.99 (m, 6H, CH$_3$); $\lambda_{\text{max}}$ (CHCl$_3$/MeOH 60:40)/nm = 591 ($\varepsilon$/M$^{-1}$cm$^{-1}$ 100700), 552 (61200), 458 (36100), 332 (30600), 285 (136000), 267 (133100); fluorescence $\lambda_{\text{max}}$ (CHCl$_3$/MeOH 60:40, $\lambda_{\text{ex}}$ = 540 nm)/nm = 625 nm, quantum yield $\Phi_\text{fl}$ (CHCl$_3$/MeOH 60:40) = 0.82±0.02; fluorescence lifetime $\tau$ (CHCl$_3$/MeOH 60:40), $\lambda_{\text{ex}}$ = 540 nm, $\lambda_{\text{em}}$ = 617 nm)/ns = 7.6±0.2.
Complexation of monotopic ligands with Zn(II) ion: $^1$H NMR titration experiments

**Fig. S1** Aromatic regions of $^1$H NMR spectra recorded at different ligand/Zn(II) ion ratios (2:0 to 2:1) at 298 K: a) For the monotopic ligand 7 and zinc triflate in CDCl$_3$/CD$_3$OD (60:40, 5 mM) from free ligand 7 (upper spectrum) to dimer (7)$_2$Zn(OTf)$_2$ (bottom); b) for the monotopic ligand 8 and zinc triflate in CDCl$_3$/CD$_3$OD (60:40, 3.5 mM) from free ligand 8 (upper spectrum) to dimer (8)$_2$Zn(OTf)$_2$ (bottom). The ratio of 7:Zn(II) ion (a) or 8:Zn(II) ion (b) is indicated on the respective spectrum. Signals for H3',5' protons are marked with # and those of H6,6'' protons with *.
Supramolecular polymerization of ditopic ligand 4a by Zn(II) ion coordination: $^1$H NMR titration experiments

**Fig. S2** Aromatic regions of $^1$H NMR spectra recorded at different ligand/Zn(II) ion ratios for the bis(tpy)-PBI ligand 4a and zinc triflate in CDCl$_3$/CD$_3$OD (60:40, 3.5 mM) at 298 K from free ligand 4a (upper spectrum, left) to polymer 10 (bottom, left) and the fragmented form 12 (bottom, right). The ratio of ligand 4a/Zn(II) ion is indicated on the respective spectrum.
**1H DOSY NMR investigations**

To provide further evidence for the formation of coordination polymers by Zn(II)-ion-mediated self-assembly of ditopic ligands 3 and 4a, 1H NMR diffusion-ordered spectroscopy (DOSY) experiments were performed. DOSY NMR spectroscopy has recently been successfully applied to characterize supramolecular coordination polymers, whose labile and dynamic nature quite often limits the success of conventional techniques for their characterization. The DOSY spectra were measured in chloroform-d/methanol-d4 (60:40) mixture at 298 K first only for the ditopic ligands 3 and 4a without Zn(OTf)2, and then after addition of one equivalent of Zn(OTf)2 to the solution of the respective ligand and subsequently after the addition of 2 equivalents of zinc(II) triflate. The 1H DOSY NMR spectra for ditopic ligands 3 and 4a are shown in Fig. S3a and S3d. The ditopic ligand 3 with a molecular weight of 991.6 g/mol shows a diffusion coefficient of $D = 3.76 \times 10^{-10}$ m$^2$s$^{-1}$ ($\log(D/m^2s^{-1}) = -9.42$) and the bis(tpy)-PBI ligand 4a with a higher molecular weight of 1670.3 g/mol exhibits a little smaller diffusion coefficient of $D = 3.47 \times 10^{-10}$ m$^2$s$^{-1}$ ($\log(D/m^2s^{-1}) = -9.46$). A significant decrease of the $D$ values to $D = 7.19 \times 10^{-11}$ m$^2$s$^{-1}$ ($\log(D/m^2s^{-1}) = -10.14$) and $5.84 \times 10^{-11}$ m$^2$s$^{-1}$ ($\log(D/m^2s^{-1}) = -10.23$), respectively, was observed when one equivalent of Zn(OTf)2 was added to 3 or 4a (see Fig. S3b and S3e). These diffusion coefficient values are one order of magnitude smaller than those of the respective ditopic monomers, indicating formation of coordination polymers upon addition of 1 equivalent of Zn(OTf)2.

When an excess amount of Zn(II) ion was added, a strong increase of the diffusion coefficients was observed, pointing at the fragmentation of the coordination polymers to oligomeric species with smaller molecular weight (Fig. S3c and S3f). At a 1:2 stoichiometry of ligand/zinc(II) ion, the diffusion coefficients are increased to $D = 2.22 \times 10^{-10}$ m$^2$s$^{-1}$ ($\log(D/m^2s^{-1}) = -9.65$) and $2.45 \times 10^{-10}$ m$^2$s$^{-1}$ ($\log(D/m^2s^{-1}) = -9.61$), which are pretty close to the values for monomeric ligands 3 and 4a.
respectively, suggesting fragmentation of polymers into monomeric complexes 11 and 12.

**Fig. S3** Aromatic regions of the $^1$H DOSY NMR spectra for bis(tpy)-PBI ligands 3 (a) and 4a (d), supramolecular polymers 9 (b) and 10 (e), and complexes 11 (c) and 12 (f) in chloroform-d/methanol-d$_4$ (60:40) at 298 K; [3] = 4.9×10$^{-3}$ M, [4a] = 3.6×10$^{-3}$ M. The diffusion coefficients $D$ (m$^2$s$^{-1}$) are plotted in a logarithmic scale ($\log(D$/m$^2$s$^{-1}$)) against the chemical shift $\delta$. The signal of residual chloroform can be seen at 7.51 ppm ($\log(D$/m$^2$s$^{-1}) = -8.65$).
UV-vis spectra of monotopic PBI ligands 7 and 8, and their dimers \((7)_{2}\text{Zn(OTf)}_{2}\) and \((8)_{2}\text{Zn(OTf)}_{2}\)

**Fig. S4** UV-vis absorption spectra of a) monotopic PBI ligand 7 (solid line) and dimer \((7)_{2}\text{Zn(OTf)}_{2}\) (dashed line), and b) monotopic PBI ligand 8 (solid line) and dimer \((8)_{2}\text{Zn(OTf)}_{2}\) (dashed line) in CHCl₃/MeOH (60:40) at 25 °C.
UV-vis titration spectra of ditopic PBI ligands 3 and 4a with Zn(II) triflate

Fig. S5 UV-vis titration spectra of ditopic PBI ligand 3 (upper) and 4a (bottom) (c = 1×10^{-5} M) with zinc(II) triflate in CHCl₃/CH₃CN (60:40) at 25 °C. The arrows indicate the spectral changes with increasing amounts of Zn(II) ions.
Scanning tunneling microscopy and current imaging tunneling spectroscopy measurements

**Fig. S6** 30 nm × 30 nm STM scan of polymer 10 attached to a HOPG defect. Bias voltage: 100 mV; tunneling current setpoint: 30 pA. Width of the chain varies between 1.9-2.5 nm. The internal structure was not explored.
**Fig. S7** (a) UV-vis spectra of self-assembled alternate multilayers [Quartz/PEI/(PSS/9)_6/(PSS/10)_6]. The inset shows the absorbance at the absorption peaks 330 (■), 480 (○), 590 (▲), and 700 nm (●) as a function of the number of layers of coordination polymers 9 and 10. The arrows indicate the change of absorbance with increasing number of layers. (b-d) Height AFM images of quartz substrate (b), PEI/PSS
layer (c), and film after deposition of coordination polymers (d); the white scale bar in all images is 1 µm; z data scales are 15 (b), 70 (c), and 25 nm (d). The insets in (b-d) depict AFM angle view images.

(e) Schematic representation of layer-by-layer film prepared in alternate fashion.

References


