Supporting Information

Supramolecular coordination polymers using a close to 'V-shaped' fluorescent 4-amino-1,8-naphthalimide Tröger's base scaffold

Sankarasekaran Shanmugaraju,*a Chris S. Hawes,^a Aramballi J. Savyasachi,^a Salvador Blasco,^a Jonathan A. Kitchen,^b and Thorfinnur Gunnlaugsson*^a

^aSchool of Chemistry and Trinity Biomedical Sciences Institute (TBSI), Trinity College Dublin, The University of Dublin, Dublin 2, Ireland.

^bChemistry, Faculty of Natural and Environmental Sciences, University of Southampton-Highfield, Southampton, SO17 1BJ, UK.

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Experimental section

Materials and methods. All reagents, solvents, and starting materials were purchased from Sigma-Aldrich, Merck, or Fisher Scientific, were of reagent grade and were used as received. Solvents used were HPLC grade unless otherwise stated. 4-Nitro-1,8-naphthalic anhydride, 3-Picolylamine, Palladium on carbon (10 wt % loading), Paraformaldehyde, Trifluoroacetic acid and all metal salts were purchased from Sigma-Aldrich and used as received. Deuterated solvent $(CD_3)_2SO$ used for NMR analyses were purchased from Sigma-Aldrich or Apollo Scientific. *N*-[(3-pyridyl)methyl]-4-nitro-1,8-naphthalimide precursor was synthesized following the procedure reported in the literature.^{1,2}

Melting point was determined using an Electrochemical IA9000 digital melting point apparatus in an unsealed capillary tube.

The elemental analysis for C, H and N were performed on an Exeter analytical CE-450 elemental analyzer at University College Dublin (UCD).

FT-IR spectra were recorded in the range 4000–550 cm⁻¹ on a Perkin-Elmer spectrometer equipped with a universal ATR sampling accessory.

All NMR spectra were recorded on a Bruker-DPX-Avance spectrometer operating at 400/600 MHz for ¹H NMR and 100/150 MHz for ¹³C NMR in commercially available deuterated solvent. Chemical shifts are reported in parts-per million (ppm) relative to the internal solvent $(CD_3)_2SO = 2.5$ ppm signal. All NMR data were processed with Bruker Win-NMR 5.0, Topspin and MestReNova softwares. Multiplicities were abbreviated as follows: singlet (s), doublet (d), doublet of doublet (dd), triplet (t), multiplet (m).

The solid-state CP/MAS ¹³C-NMR spectrum of the degraded **TB-Cd-CP** was acquired using a 3.2 mm double-resonance MAS probe. The spectrum was acquired under magic angle spinning (MAS) at 60 kHz, if not otherwise specified, using ramped-amplitude cross-polarization, and SPINAL64 decoupling with a ¹H-decoupling field of about 80 kHz. A 3 ms contact time and a pulse delay of 5 s were used. Chemical shifts were calibrated setting the ¹³C low field signal of adamantane to 38.48 ppm.

APCI-ESI mass spectra were acquired on a Bruker microTOF-Q III spectrometer interfaced to a Dionex UltiMate 3000 LC or direct insertion probe. The instrument was operated in positive or negative mode as required. Agilent tuning mix APCI-TOF was used to calibrate the system. The

m/z values were recorded over a range of 100-1600. MicroTof control and HyStar software were used to carry out the analysis. HPLC-grade CH₃CN or CH₃OH or DMSO were used as carrier solvents.

Thermogravimetric analysis (TGA) were performed on an analyzer equipped with an ultramicrobalance with a sensitivity of 0.1 μ g. The temperature range was from 25°C to 800°C with a scan rate of 10°C/min under N₂ purge.

X-ray powder diffraction patterns were collected using a Bruker D2 Phaser instrument with Cu K α radiation ($\lambda = 1.5418$ Å). Samples were ground and mounted on silicon sample holders, and data were collected in the 2 θ range 5–55° at room temperature. The patterns were compared with those simulated from the single-crystal data collected at 100 K

Morphological features were imaged by field-emission scanning electron microscopy (FE-SEM) using Zeiss ULTRA Plus with an SE2 or in-lens detector in the Advanced Microscopy Laboratory, CRANN, Trinity College Dublin. The samples for FE-SEM were prepared by drop-casting the suspension of **TB-Co-CP** and **TB-Cd-CP** from their corresponding reaction mixture on silica wafers, then coated with Au and dried under vacuum before the imaging.

UV-visible absorption spectra were recorded in 1 cm quartz cuvettes (Hellma) on a Varian Cary 50 spectrometer. Baseline correction was applied for all spectra.

Emission spectra were recorded on a Varian Cary Eclipse Fluorimeter. The temperature was kept constant throughout the measurements at 298 K by using thermostated unit block. Solid-state emission spectra were measured at room temperature with powdered samples casted on a quartz plates.

Confocal fluorescence microscopy images of L and **TB-Cd-CP** were obtained using Leica SP8 STED confocal microscopy with a 40X oil immersion lens. Image analysis was performed using FluoView Version 7.1 Software.

Synthesis and Characterization of Ligand L

N-[(3-pyridyl)methyl]-4-amino-1,8-naphthalimide (1): *N*-[(3-pyridyl) methyl]-4-nitro-1,8naphthalimide (200 mg, 0.60 mmol) was reduced by catalytic hydrogenation using Pd/C (10%, 20 mg) at 3 atm of H₂ in DMF (10 mL) for 12 h. The reaction mixture was then filtered through celite and washed several times with fresh DMF until the washings ran clear. The solvents were removed under reduced pressure to isolate compound **1** (174 mg, 0.57 mmol, 96%) as an orange solid after trituration with cold-diethyl ether. Melting point 295–297 °C (decomp.). HRMS (APCI) *m/z*: calcd for C₁₈H₁₄N₃O₂ [M+H⁺] 304.1086, found 304.1083; ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.65-8.60 (1H, dd, *J* = 8.4 Hz, Ar-H), 8.46 (1H, s, Pyridyl-H), 8.44-8.43 (1H, d, *J* = 4.8 Hz, Ar-H), 8.23-8.21 (1H, d, *J* = 8.4 Hz, Ar-H), 7.73-7.71 (1H, d, *J* = 8.0 Hz, Ar-H), 7.69-7.65 (1H, t, *J* = 8.0 Hz, Ar-H), 7.52 (2H, s, Ar-NH₂), 7.34-7.30 (1H, dd, *J* = 7.9, 4.8 Hz, Pyridyl-H), 6.87-6.85 (1H, d, *J* = 8.4 Hz, Pyridyl-H), 5.24 (2H, s, Pyridyl-CH₂); ¹³C NMR (100 MHz, (CD₃)₂SO) δ 164.34, 163.34, 153.52, 149.70, 148.65, 135.89, 134.75, 134.06, 131.79, 130.32, 130.09, 124.49, 123.97, 122.01, 119.85, 108.74, 107.59, 31.13; FT-IR ν_{max} (ATR, cm⁻¹) 3660, 2980, 2890, 1703, 1656, 1624, 1579, 1526, 1478, 1462, 1428, 1377, 1339, 1318, 1232, 1179, 1166, 1120, 1099, 1028, 976, 955, 934, 883, 870, 829, 787, 761, 732, 713, 670, 645, 631, 612, 585, 554.

Bis-[N-(3-pyridyl)methyl)]-9,18-methano-1,8-naphthalimide-[b,f][1,5]diazocine (L): Compound 1 (200 mg, 0.66 mmol, 1 equiv.) and paraformaldehyde (30 mg, 0.99 mmol, 1.5 equiv.) were flushed with argon. Trifluoroacetic acid (4 mL) was added at 0°C and the solution was stirred at room temperature for 12 h under an inert atmosphere. The reaction mixture was added dropwise to aqueous ammonium hydroxide (100 mL) at 0° C and ammonia solution was added until a pH > 10 was achieved. Dichloromethane $(2 \times 200 \text{ mL})$ was added and the organic layer was extracted and washed with saturated NaHCO₃ (2×100 mL), brine (2×100 mL) and H₂O (2×100 mL). The solution was dried over MgSO₄ and the solvents were removed under reduced pressure to isolate compound L (186 mg, 0.27 mmol, 83%) as a bright yellow solid after trituration with cold-diethyl ether. Anal. Calcd (%) for C₃₉H₂₆N₆O₄·0.4CH₂Cl₂: C, 69.94; H, 3.99; N, 12.42: Found C, 70.21; H, 3.91; N, 12.53. Melting point 283–285 °C (decomp.). HRMS (APCI) m/z: calcd for C₃₉H₂₇N₆O₄ $[M+H^+]$ 643.2094, found 643.2069; ¹H NMR (600 MHz, (CD₃)₂SO) δ 8.75-8.73 (2H, d, J = 8.9Hz, Ar-H), 8.53 (2H, s, Pyridyl-H), 8.49-8.48 (2H, d, J = 7.3 Hz, Ar-H), 8.40-8.39 (2H, d, J = 6.2 Hz, Pyridyl-H), 8.13 (2H, s, Ar-H), 8.00-7.93 (2H, m, Ar-H), 7.64-7.62 (2H, d, J = 8.0 Hz, Pyridyl-H), 7.26-7.23 (2H, dd, J = 7.9, 4.8 Hz, Pyridyl-H), 5.17 (4H, s, Pyridyl-CH₂), 5.18-5.15 (2H, d, J = 17.4 Hz, NCH₂), 4.72 (2H, s, NCH₂), 4.68-4.65 (2H, d, J = 17.4 Hz, NCH₂); ¹³C NMR (150 MHz, $(CD_3)_2SO$ δ 163.97, 163.39, 149.82, 149.53, 148.73, 135.65, 133.45, 131.48, 130.97, 129.87, 128.05, 127.68, 127.22, 126.71, 123.93, 122.76, 117.94, 66.52, 57.26, 4100; FT-IR v_{max} (ATR, cm⁻¹) 3038, 2156, 1971, 1702, 1654, 1624, 1594, 1581, 1517, 1478, 1460, 1428, 1405, 1378, 1335, 1319, 1231, 1180, 1168, 1120, 1098, 1027, 975, 934, 869, 828, 786, 761, 732, 711, 674, 630, 613, 586.

poly-[CoCl₂(L)].2.666 H₂O (TB-Co-CP): Compound L (20 mg, 29.6 µmol) and cobalt(II) chloride hexahydrate (7.0 mg, 29.6 µmol) were combined in 2 mL of DMF. The mixture was briefly sonicated, capped, and heated at 100°C for 48 h. Green-rod shaped crystals were isolated by filtration, washed with fresh DMF (2×2 mL) and dried in air. Yield: 8 mg (41%). Anal. Calcd (%) for C₃₉H₂₆N₆O₄Cl₂Co·2²/₃H₂O: C, 57.09; H, 3.85; N, 10.24: Found C, 56.84; H, 3.61; N, 10.63. FT-IR v_{max} (ATR, cm⁻¹) 2980, 1695, 1648, 1617, 1596, 1569, 1510, 1484, 1457, 1436, 1401, 1373, 1350, 1334, 1314, 1257, 1232, 1169, 1156, 1130, 1104, 1088, 1051, 1026, 966, 913, 871, 844, 812, 792, 782, 767, 757, 711, 703, 689, 668, 660, 621, 591, 580, 569, 555.

poly-[Cd(L)₂(NO₃)_{0.5}(H₂O)_{1.5}].1.5(NO₃)·4CH₂Cl₂ (TB-Cd-CP): Compound L (20 mg, 29.6 μmol) and cadmium(II) nitrate tetrahydrate (9.1 mg, 29.6 μmol) were combined in a mixture of CH₂Cl₂-CH₃OH-CH₃CN (3 mL in 1:1:1 volume ratio) and the mixture was kept for slow evaporation at room temperature. After 72 hours, yellow block shaped crystals of the product were isolated by filtration, washed with CH₃CN (2 × 3 mL) and dried in air. Yield: 11 mg (55%). Anal. Calcd (%) for C₇₈H₅₂N₁₄O₁₄Cd.1.5H₂O·4CH₂Cl₂: C, 52.15; H, 3.36; N, 10.38: Found C, 51.73; H, 2.91; N, 10.68. CP-MAS ¹³C-NMR: $\delta_{\rm C}$ (400 MHz) 163, 149, 132, 126, 121, 117, 66, 57, 40. FT-IR $\nu_{\rm max}$ (ATR, cm⁻¹) 3064, 2981, 2159, 1968, 1701, 1656, 1622, 1595, 1580, 1516, 1478, 1460, 1428, 1405, 1378, 1337, 1318, 1257, 1230, 1181, 1169, 1120, 1099, 1027, 976, 935, 914, 870, 828, 787, 761, 733, 711, 670, 630, 610, 586, 554, 529.

X-Ray Crystallography

All diffraction data were collected with a Bruker Apex-II Duo instrument using microfocus Cu Ka radiation ($\lambda = 1.54178$ Å, **TB-Co-CP**) or graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å, **TB-Cd-CP**). All data collections were carried out at 120 K or 100 K with sample temperature maintained using a Cobra cryostream. Data collection and processing were carried out using the Bruker APEX-3 suite of programs³ with multi-scan absorption corrections applied using SADABS.⁴ All data were solved on F^2 using SHELXT within the OLEX-2 software package,^{5,6} and refined using full-matrix least squares procedures with SHELXL-2014.⁷ The functions minimized were $\Sigma w(F_0^2 - F_c^2)$, with $w = [\sigma^2 (F_0^2) + aP^2 + bP]^{-1}$, where $P = [max(F_0)^2 + 2F_c^2]/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined with a riding model, with U_{eq} equal to 1.2 or 1.5 times the isotropic equivalent of the carrier atom, where appropriate. For both structures, the SQUEEZE routine within PLATON was employed^{8,9} to provide more representative refinement statistics for

the framework atoms in the presence of large areas of diffuse electron density, which was identified using supporting methods (see text). In the case of **TB-Cd-CP**, significant disorder was present involving the coordinating and non-coordinating nitrate anions, and these were modelled in chemically representative positions using U_{ij} and position/distance restraints and constraints as necessary to provide a chemically sensible model. The mixed nitrato/aqua coordination of Cd₂ was modelled with two site-shared oxygen atoms (total occupancy 1.0), constrained with x, y, z and U_{ij} equal, representing a statistical mixture of substitution throughout the crystal. Hydrogen atoms for the aqua ligands in this structure could not be sensibly modelled, but were nonetheless included in the moiety formula. Specific refinement strategies are outlined in the combined crystallographic (CCDC: 1568817–1568818) information file.

References:

- 1. J. I. Lovitt. C. S. Hawes, A. D. Lynes, B. Haffner, M. E. Mobius and T. Gunnlaugsson. T, *Inorg. Chem. Front.*, 2017, **4**, 296-308.
- 2. H. Shaki, K. Gharanjig, S. Rouhani and A. Khosravi. J. Photochem. Photobiol. A., 2010, **216**, 44-50.
- 3. Bruker APEX-3, Bruker-AXS Inc., Madison, WI, 2016.
- 4. SADABS, Bruker-AXS Inc., Madison, WI, 2016.
- 5. G. M. Sheldrick, Acta Crystallogr. Sect. A. 2015, 71, 3-8.
- 6. G. M. Sheldrick, Acta Crystallogr. Sect. C. 2015, 71, 3-8.
- 7. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.
- 8. A. L. Spek, Acta Crystallogr. Sect. C. 2015, 71, 9-18.
- 9. A. L. Spek, Acta Crystallogr. Sect. D. 2009, 65, 148-155.



Fig. S1. ¹H NMR spectrum of 1 (400 MHz, DMSO-d₆).



Fig. S2. ¹³C NMR spectrum of **1** (100 MHz, DMSO-d₆).



Fig. S3. HRMS spectrum of 1.



Fig. S4. ¹H NMR spectrum of L (600 MHz, DMSO-d₆).



Fig. S5. ¹³C NMR spectrum of **2** (150 MHz, DMSO-d₆).



Fig. S6. HRMS spectrum of L.



Fig. S7. Infrared spectrum of 1.



Fig. S8. Infrared spectrum of L.



Fig. S9. UV-visible absorption spectra of L (24 μ M) in different polar solvents.

Table S1. Summary of solution-phase UV/vis absorption and emission spectral data for L in different polar solvents.

Solvent	Polarity Index (P')	Absorption maxima λ_{max} (nm)	$\begin{array}{c} \text{Molar extinction} \\ \text{coefficient} \\ \epsilon (10^3) \text{M}^{-1} \text{cm}^{-1} \\ [\lambda_{\text{max}} (\text{nm})] \end{array}$	Fluorescence emission maxima λ_{max} (nm)	Stokes Shift (nm)
Toluene	2.4	347, 386	5.52 (386)	469	83
DCM	3.1	347, 386	24.40 (386)	498	112
THF	4.0	346, 385	19.29 (385)	505	120
ACN	5.8	346, 385	13.64 (386)	515	130
DMF	6.4	345, 390	19.25 (390)	521	131
DMSO	7.2	348, 391	18.84 (391)	524	133



Fig. S10. Histogram plot of Cl-Co-Cl angles in crystallographically determined 4-coordinate [CoN2Cl2]-type coordination spheres (n = 494) for complex **TB-Co-CP**. Data from the Cambridge Structural Database version 5.38, May 2017.



Fig. S11. The packing of adjacent chains of complex **TB-Co-CP**, with a single chain highlighted in pink. Hydrogen atom and pyridyl group disorder are omitted for clarity.



Fig. S12. X-ray powder diffraction pattern of complex **TB-Co-CP** (measured at room temperature, blue) compared with the pattern simulated from the single crystal data (measured at 100K, red). The simulated data is presented with FWHM = $0.2 \degree$ to appropriately simulate the partial loss of crystallinity occurring upon drying.



Fig. S13. Thermogravimetric analysis for TB-Co-CP.



Fig. S14. Extended structure of **TB-Cd-CP** viewed parallel to the chain axis, showing interaction between adjacent chains and the associated solvent channels, with a single chain highlighted. All hydrogen atoms are omitted for clarity.



Fig. S15. Thermogravimetric analysis for TB-Cd-CP.



Fig. S16. X-ray powder diffraction pattern of complex **TB-Cd-CP** (measured at room temperature, blue) compared with the pattern simulated from the single crystal data (measured at 100 K, red), showing the loss of crystallinity accompanying the drying process.



Fig. S17. (A) The solid-state (CP-MAS, 400 MHz) ¹³C NMR spectrum obtained after drying a sample of **TB-Cd-CP**. (B) The ¹³C NMR (DMSO-d₆, 600 MHz) spectrum of **L**.



Fig. S18. FESEM images of complex (A) **TB-Co-CP** and (B) **TB-Cd-CP** obtained from the film casted from reaction mixture.



Fig. S19. Normalized fluorescence emission spectra obtained by dispersing the decomposed solid **TB-Cd-CP** in different solvents (Inset: corresponding photographs).

Identification code	ТВ-Со-СР	TB-Cd-CP
Empirical formula	$C_{39}H_{26}Cl_2CoN_6O_4$	C ₇₈ H ₅₅ CdN ₁₄ O _{15.5}
Formula weight	772.49	1548.76
Temperature/K	120	100
Crystal system	orthorhombic	monoclinic
Space group	Pnna	$P2_{1}/c$
a/Å	15.5714(13)	17.9643(8)
b/Å	17.6017(14)	26.5902(13)
c/Å	28.163(2)	19.4124(8)
α/°	90	90
β/°	90	115.5400(10)
γ/°	90	90
Volume/Å ³	7718.9(11)	8366.7(7)
Z	8	4
$\rho_{calc}g/cm^3$	1.329	1.23
μ/mm ⁻¹	5.147	0.329
F(000)	3160	3172
Crystal size/mm ³	$0.13 \times 0.05 \times 0.02$	$0.274 \times 0.165 \times 0.087$
Radiation	CuK α (λ = 1.54178)	MoK α ($\lambda = 0.71073$)
2\Overlap range for data collection/°	5.92 to 136.926	2.784 to 50.88
Index ranges	$-18 \le h \le 18, -21 \le k \le$	$-19 \le h \le 21, -32 \le k \le$
	$21, -33 \le l \le 33$	$31, -21 \le 1 \le 23$
Reflections collected	74215	75827
Independent reflections	$7087 [R_{int} = 0.1034,$	$15377 [R_{int} = 0.1207,$
	$R_{sigma} = 0.0530$	$R_{sigma} = 0.1168$
Data/restraints/parameters	7087/44/496	15377/48/958
Reflections Observed $[1 \ge 2\sigma(1)]$	3971	7083
Goodness-of-fit on F ²	1.045	0.992
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0862, WR_2 = 0.2580$	$R_1 = 0.0698, WR_2 = 0.1757$
	P = 0.1352 m/P -	P = 0.1624 m/P - 0.1624 m/P
Final R indexes [all data]	$1 - 0.1332, WR_2 - 0.3083$	0.2214
Largest diff. peak/hole / e Å ⁻³	1.00/-0.74	1.05/-1.09
CCDC No.	1568817	1568818

 Table S2: Crystallographic data and refinement parameters of TB-Co-CP and TB-Cd-CP.