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Electronic Supplementary Information

AzaBODIPY based coordination polymers

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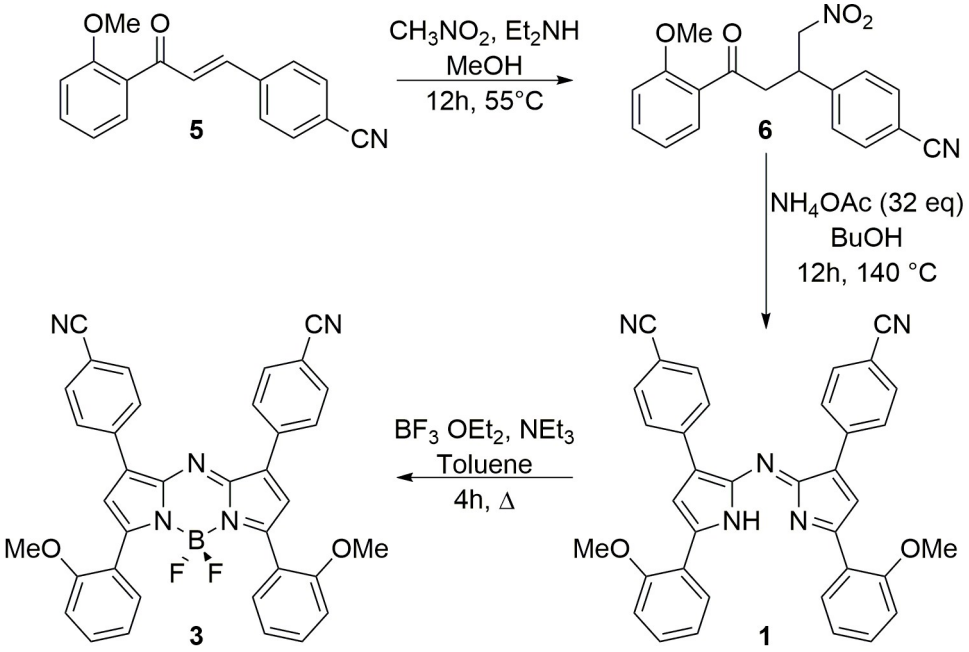

Scheme ESI1 Synthetic route for the preparation of azaBODIPY **3**.

Synthesis

Compounds **2** and **4** were synthesized as reported.[1] Chalcone **5** was prepared as described.[2] Nitromethane is a potentially explosive reagent, special care should be taken when handling it.

^{1}H- and ^{13}C-NMR spectra were recorded at 25 °C on a Bruker AV300 (300 MHz), AV400 (400 MHz) or AV500 (500 MHz) with the deuterated solvent as the internal reference. NMR chemical shifts and *J* values are given in parts per million (ppm) and in Hertz, respectively. Mass spectrometry and elemental analyses were performed by the Service commun d'analyse (University of Strasbourg). UV-visible spectra were recorded on a Perkin Elmer Lambda

650S spectrophotometer. Emission and excitation spectra were recorded on a Perkin Elmer LS 55 spectrometer.

Compound **6**: To a suspension of **5** (5.79 g, 0.028 mol) in MeOH (30 mL), Et_2NH (8.0 mL, 0.077 mol) was first added followed by dropwise addition of nitromethane (8.2 mL, 0.153 mol). The mixture was refluxed at 55 °C overnight. The yellow solution was concentrated under vacuum and 2 mL of toluene were added (to prevent explosion due to the presence of nitromethane). Purification by column chromatography (SiO_2, CH_2Cl_2) yielded the Michael addition product **6** in 77% yield (5.46 g). δ_H (300 MHz, $CDCl_3$): 7.64 (m, 3H), 7.49 (m, 1H), 7.41 (m, 2H), 6.99 (m, 2H), 4.74 (m, 2H), 4.26 (m, 1H), 3.89 (s, 3H), 3.45 (m, 2H). IR (ATR) ν/cm^{-1}: 2222.9 (νCN).

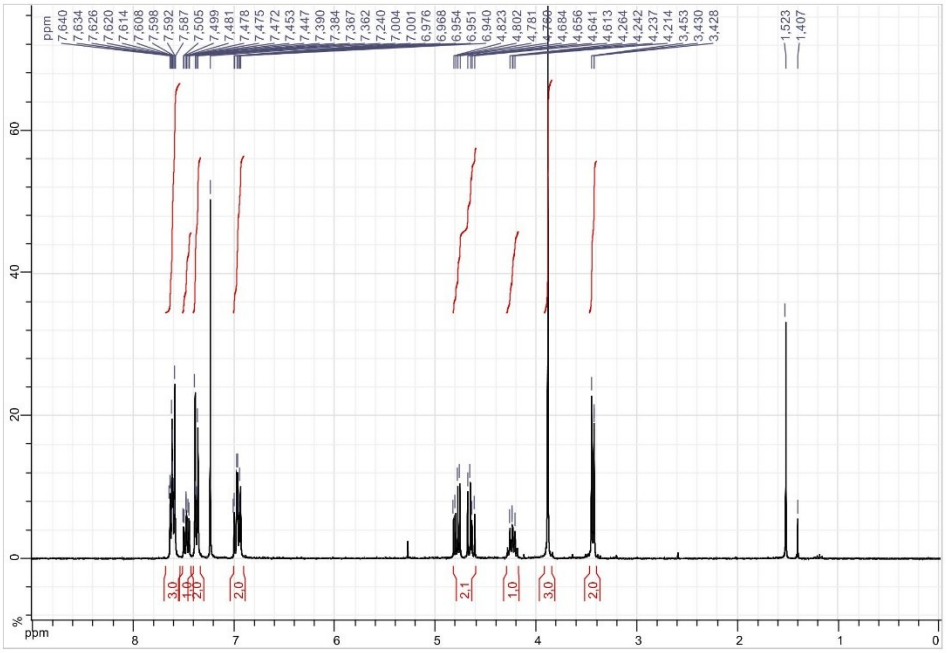

Fig. ESI1 ^{1}H-NMR spectrum of compound **6** in $CDCl_3$.

Azadipyrrin **1**: Ammonium acetate (45.7 g, 0.59 mol) was added to a solution of **6** (6 g, 0.0185 mol) in *n*-BuOH (514 mL). Upon refluxing for 4 days, the white suspension became clear and a dark blue precipitate formed. Upon filtration, **1** was obtained as a dark blue powder in 17% yield (0.90 g). Crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-pentane vapor into a $CHCl_3$ solution of **1**. δ_H (300 MHz, THF-d$_8$): 13.05 (s, 1H), 8.21 (m, 3H), 7.80 (d, J = 8.7 Hz, 2H), 7.60 (s, 1 H), 7.45 (td, J = 7.8 and 1.9 Hz, 2H), 7.17 (d, J = 8.7 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 3.99 (s, 3H). δ_C (125 MHz, THF-d8) 158.4, 154.3, 148.5, 138.7, 138.2, 131.9, 131.7, 129.2, 121.0, 120.7, 119.5, 118.4, 112.1, 111.2, 55.6.

IR (ATR) ν/cm^{-1}: 2223.1 (νCN). λ_{max}($CHCl_3$)/nm (ε/mol.L^{-1}.cm^{-1}): 349 (28200), 621 (50600). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{36}H_{26}N_5O_2$: 560.2081; found: 560.2031.

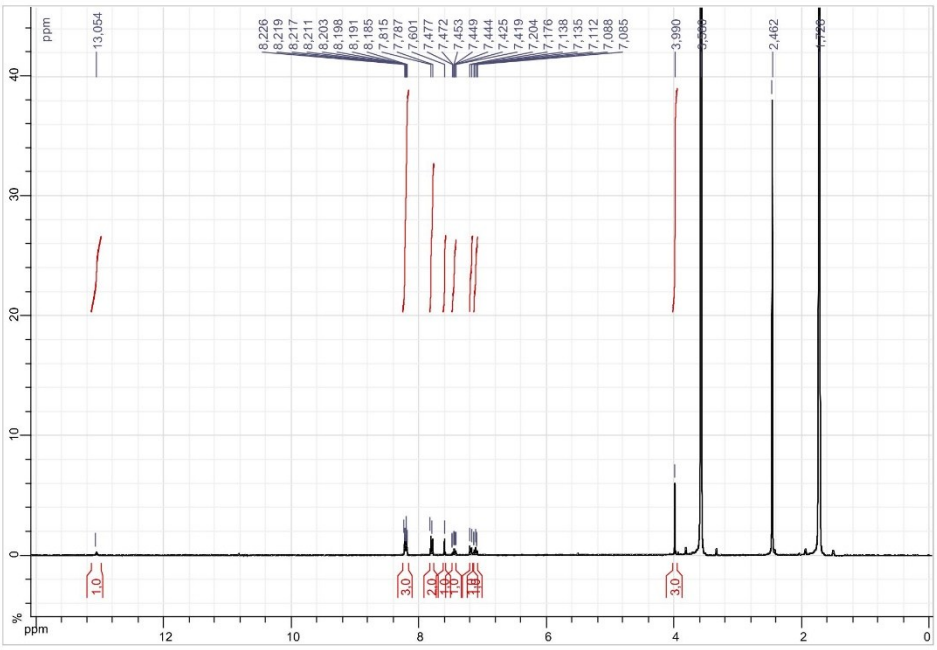

Fig. ESI2 ^{1}H-NMR spectrum of azadipyrrin **1** in THF-d_8.

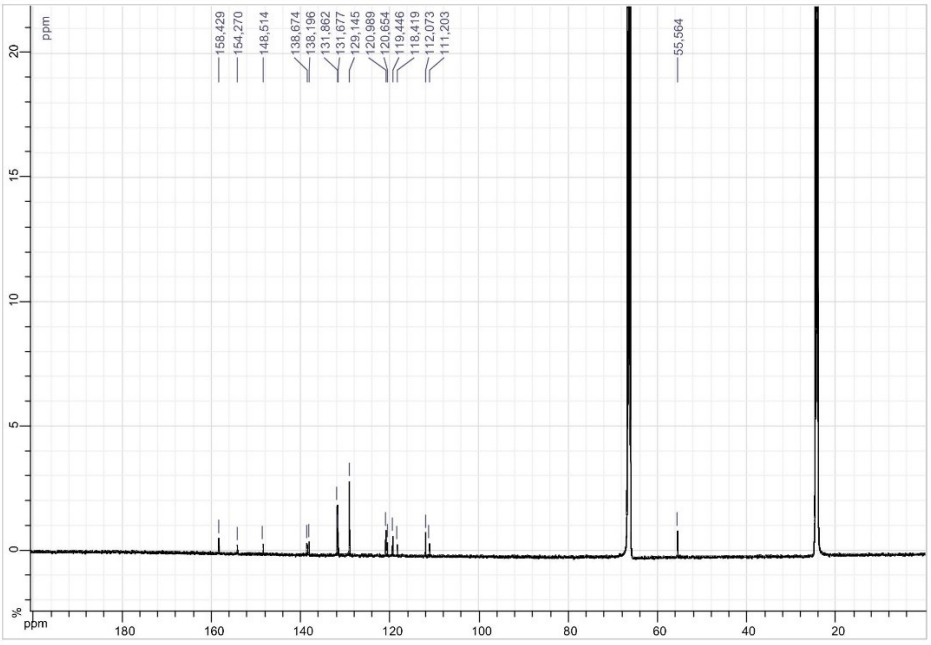

Fig. ESI3 ^{13}C-NMR spectrum of azadipyrrin **1** in THF-d_8.

AzaBODIPY **3**: To a suspension of **1** (0.80 g, 0.00143 mol) in toluene (500 mL) under argon, Et_3N (9.6 mL, 0.0715 mol) and $BF_3.OEt_2$ (17.6 mL, 0.143 mol) were added dropwise. The mixture was refluxed for 4h. $BF_3.OEt_2$ was quenched by addition of cold EtOH. Solvents were evaporated under vacuum and MeOH was added. The precipitate formed was recovered by filtration to afford **3** in 98% yield (0.78 g). Crystals suitable for X-Ray diffraction were obtained by slow diffusion of *n*-pentane into a solution of **3** in dioxane. δ_H (500 MHz, THF-d*8*): 8.25 (d, *J* = 8.5 Hz, 4H), 7.86 (m, 6H), 7.41 (m, 2H), 7.31 (s, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.97 (td, *J* = 0.8 and 7.7 Hz, 2H), 3.86 (s, 6H). δ_C (125 MHz, THF-d*8*) 159.2, 158.7, 145.6, 140.9, 137.2, 133.0, 132.8, 132.3, 130.1, 123.8, 121.3, 120.7, 118.8, 113.3, 111.8, 55.9. δ_F (280 MHz, THF-d*8*) -136.2 (q, *J* = 29.5 Hz). IR (ATR) ν/cm^{-1}: 2223.8 (*ν*CN). λ_{max}($CHCl_3$)/nm (ε/mol.L^{-1}.cm^{-1}): 331 (27800), 664 (89400). HRMS (ESI) *m/z*: $[M]^+$ calcd. for $C_{36}H_{24}BF_2N_5O_2$: 607.1992; found: 607.1993.

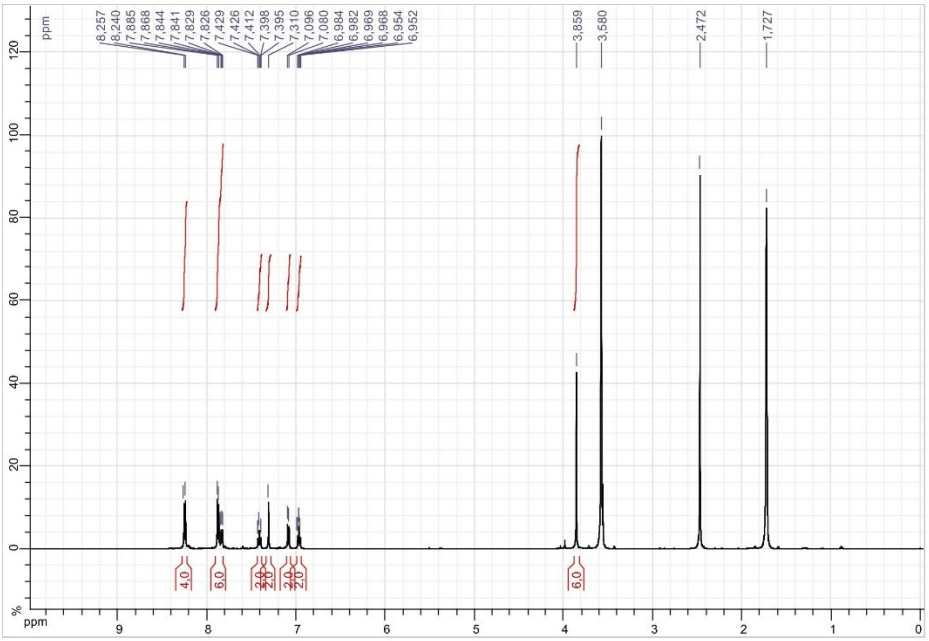

Fig. ESI4 ^{1}H-NMR spectrum of azaBODIPY **3** in THF-d$_8$.

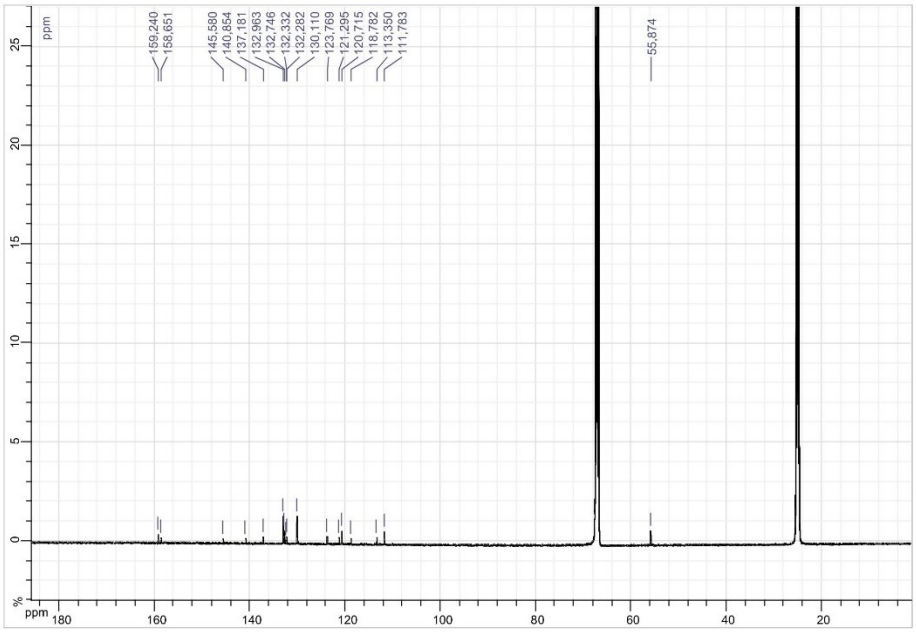

Fig. ESI5 ^{13}C-NMR spectrum of azaBODIPY **3** in THF-d_8.

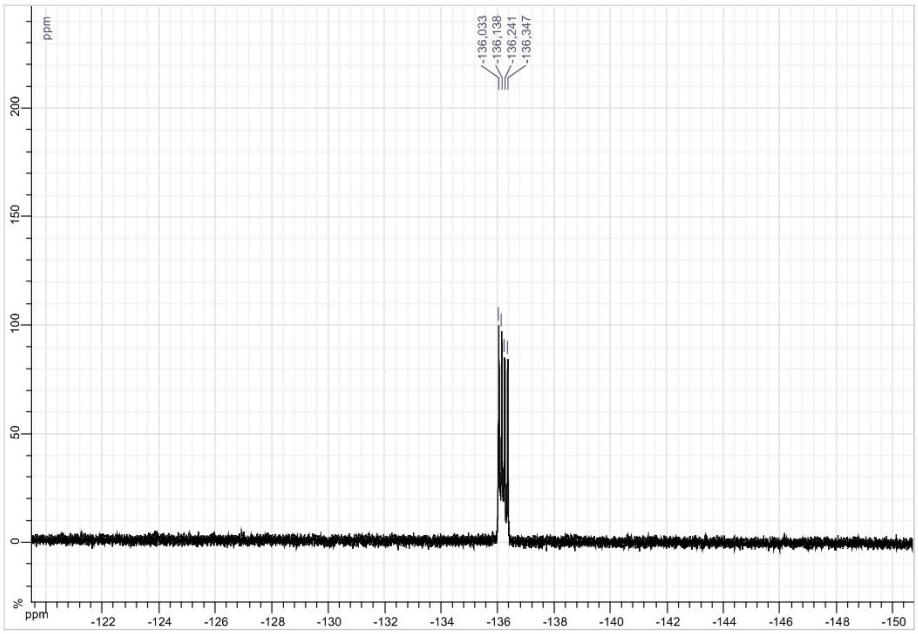

Fig. ESI6 ^{19}F-NMR spectrum of azaBODIPY **3** in THF-d_8.

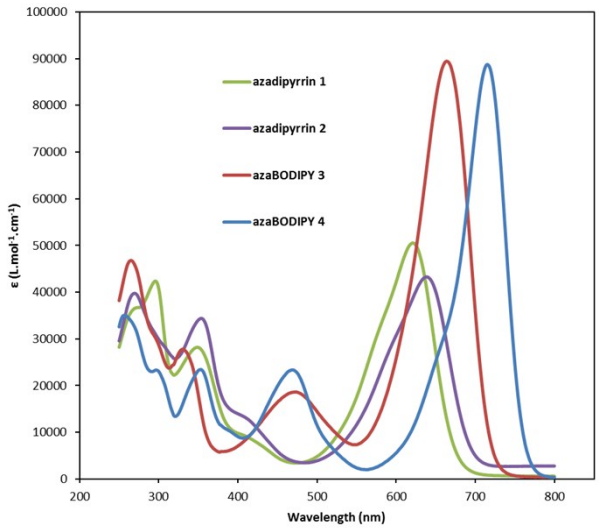

Fig. ESI 7. Absorption spectra of compounds **1**-**4** in $CHCl_3$ solution.

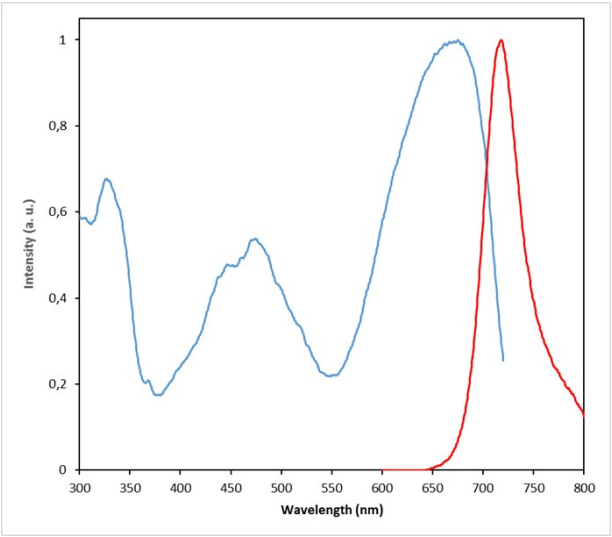

Fig. ESI 8. Excitation (blue line, λ_{em} = 718 nm) and emission (red line, λ_{ex} = 580 nm) spectra of azaBODIPY **3** in $CHCl_3$ solution.

Network **7**: A $CHCl_3$ solution (3 mL) of $Ag(BF_4)$ (4 mg, 0.021 mmol) was first layered by a 1/1 $CHCl_3$/THF (3 mL) mixture and then by a THF solution (8 mL) of azaBODIPY **3** (10 mg, 0.016 mmol). Crystals of **7** were harvested after few days. IR (ATR) ν/cm^{-1}: 2250.2 (*ν*CN). Found: C, 50.13; H, 3.17; N, 7.65. $(C_{36}H_{24}AgB_2F_6N_5O_2)_2(C_4H_8O)(CHCl_3)$ requires C, 51.50; H, 3.19; N, 7.80.

Network **8**: A $CHCl_3$ solution (3 mL) of $Ag(BF_4)$ (4 mg, 0.021 mmol) was first layered by a 1/1 $CHCl_3$/THF (3 mL) mixture and then by a THF solution (10 mL) of azaBODIPY **4** (5 mg, 0.008 mmol). Crystals of **8** were harvested after few days. IR (ATR) ν/cm^{-1}: 2244.8, 2264.9 (*ν*CN).

X-Ray diffraction

Single-crystal data (Tables ESI1 and ESI2) were collected on a Bruker SMART CCD diffractometer with Mo–Kα radiation at 173 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.[3] The hydrogen atoms were introduced at calculated positions and not refined (riding model). In the structure of **4**, one $CHCl_3$ molecule is disordered over two positions. In the structure of **7**, highly disordered THF and $CHCl_3$ molecules are present, the SQUEEZE command has been employed to account for the corresponding electron density.[4] Furthermore, the Ag(I) cation was found to be disordered over two positions. Refinement on data collected on different crystals with various exposure time consistently led to a structure featuring this positional disorder of the metal cation. In the structure of **8**, one THF molecule is disordered over two positions. The hydrogen atoms on this molecule have not been introduced but are taken into account in the compound formula.

CCDC 1522701-1522705 contain the supplementary crystallographic data for compounds **1**, **3**-**4** and **7**-**8**. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

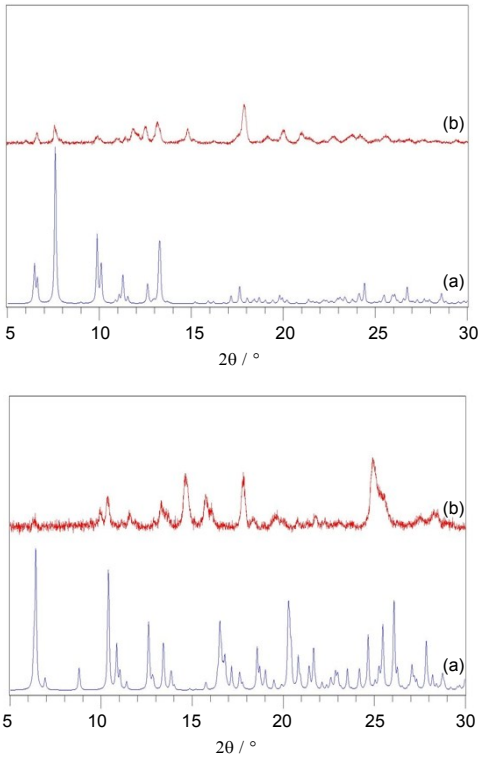

Fig. ESI9 Simulated (a) and experimental (b) PRXD pattern for network **7** (top) and **8** (bottom) showing the loss of crystallinity of the compounds upon removal from the mother liquor.

Table ESI1 Crystallographic data for compounds **1**, **3** and (**4**)$_2$(CHCl$_3$)

	1	**3**	(**4**)$_2$(CHCl$_3$)
Formula	$C_{36}H_{25}N_5O_2$	$C_{36}H_{24}BF_2N_5O_2$	$C_{73}H_{49}B_2Cl_3F_4N_{10}O_4$
FW	559.61	607.41	1334.19
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a / Å	9.1444(8)	16.9698(8)	16.8878(11)
b / Å	12.2700(8)	12.9677(7)	13.8408(13)
c / Å	13.4648(10)	13.8541(8)	14.4153(13)
α / °	110.287(2)		
β / °	95.118(3)	108.953(2)	109.557(2)
γ / °	90.687(3)		
V / Å^3	1409.92(19)	2883.4(3)	3175.1(5)
Z	2	4	2
T / K	173(2)	173(2)	173(2)
μ/ mm^{-1}	0.084	0.097	0.217
Refls. coll.	22455	33370	35368
Ind. refls. (Rint)	7512 (0.0539)	8394 (0.0520)	9068 (0.0767)
R_1 (I>2σ(I))[a]	0.0770	0.0642	0.0761
wR_2 (I>2σ(I))[a]	0.1371	0.1339	0.1762
R_1 (all data)[a]	0.1637	0.1289	0.1405
wR_2 (all data)[a]	0.1643	0.1576	0.2059
GOF	1.036	1.032	1.039

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$

Table ESI2 Crystallographic data for compounds **7** and **8**

	7	**8**
Formula	$C_{36}H_{24}AgB_2F_6N_5O_2$	$C_{148}H_{104}Ag_2B_6F_{16}N_{20}O_9$
FW	802.09	2891.11
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pnna*
a / Å	29.3110(13)	14.4266(5)
b / Å	15.3218(5)	16.3190(6)
c / Å	18.7508(7)	27.6414(11)
β / °	110.666(3)	
V / Å^3		6507.6(4)
Z	8	2
T / K	173(2)	173(2)
μ/ mm^{-1}	0.576	0.394
Refls. coll.	96561	71454
Ind. refls. (Rint)	11741 (0.0317)	9549 (0.0878)
R_1 (I>2σ(I))[a]	0.0532	0.0635
wR_2 (I>2σ(I))[a]	0.1600	0.1782
R_1 (all data)[a]	0.0843	0.1281
wR_2 (all data)[a]	0.1822	0.2147
GOF	1.042	1.054

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$

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