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Supplementary Information for

A Self-Assembled Supramolecular Capsule That Cocrystallizes with 1,4-Disubstituted Benzene Derivatives

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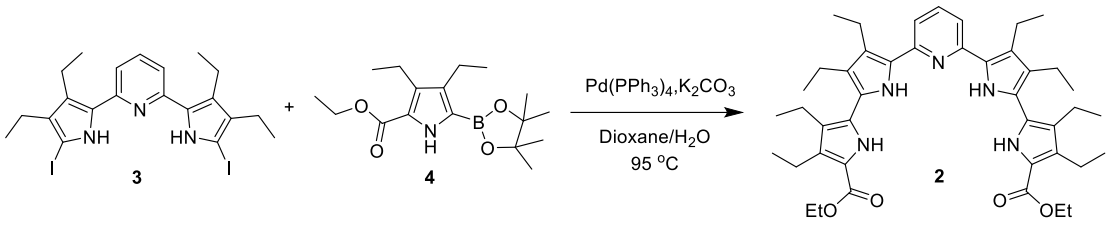
Contents

1. Synthetic experimental



Compound **2**

To a 250 mL round bottom flask containing **3** (1 g, 1.75 mmol), **4** (1.4 g, 4.36 mmol), $Pd(PPh_3)_4$ (101.15 mg，0.0875 mmol) and K_2CO_3 (1.21 g，8.75 mmol), 40 mL dioxane and 10 mL H_2O were injected under N_2 atmosphere before the reaction mixture was stirred for 24 h at 95℃. After being cooled to room temperature, the mixture was extracted with dichloromethane and the organic layer was collected. The solvent was then removed and the crude mixture was purified using silica chromatography (petroleum ether: ethyl acetate) to give **2** as a yellowish solid in 60% yield.

HRMS (ESI, $[M+H]^+$) Calculated for $C_{43}H_{57}N_5O_4$: 708.4483. Found: 708.4489.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 4H), 8.76 (s, 4H), 7.67 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 4H), 4.28 (q, *J* = 7.1 Hz, 8H), 2.79 (dq, *J* = 22.2, 7.4 Hz, 16H), 2.49 (dq, *J* = 21.5, 7.6 Hz, 16H), 1.33 (t, *J* = 7.2 Hz, 12H), 1.29 (t, *J* = 7.4 Hz, 12H), 1.18 (t, *J* = 7.4 Hz, 12H), 1.12 (t, *J* = 7.5 Hz, 12H), 1.01 (t, *J* = 7.5 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.30, 149.90, 137.26, 133.54, 127.05, 126.21, 125.30, 125.11, 120.72, 118.12, 115.46, 59.84, 18.52, 18.35, 17.78, 17.73, 16.53, 16.29, 15.74, 15.41, 14.46.

2. NMR spectra

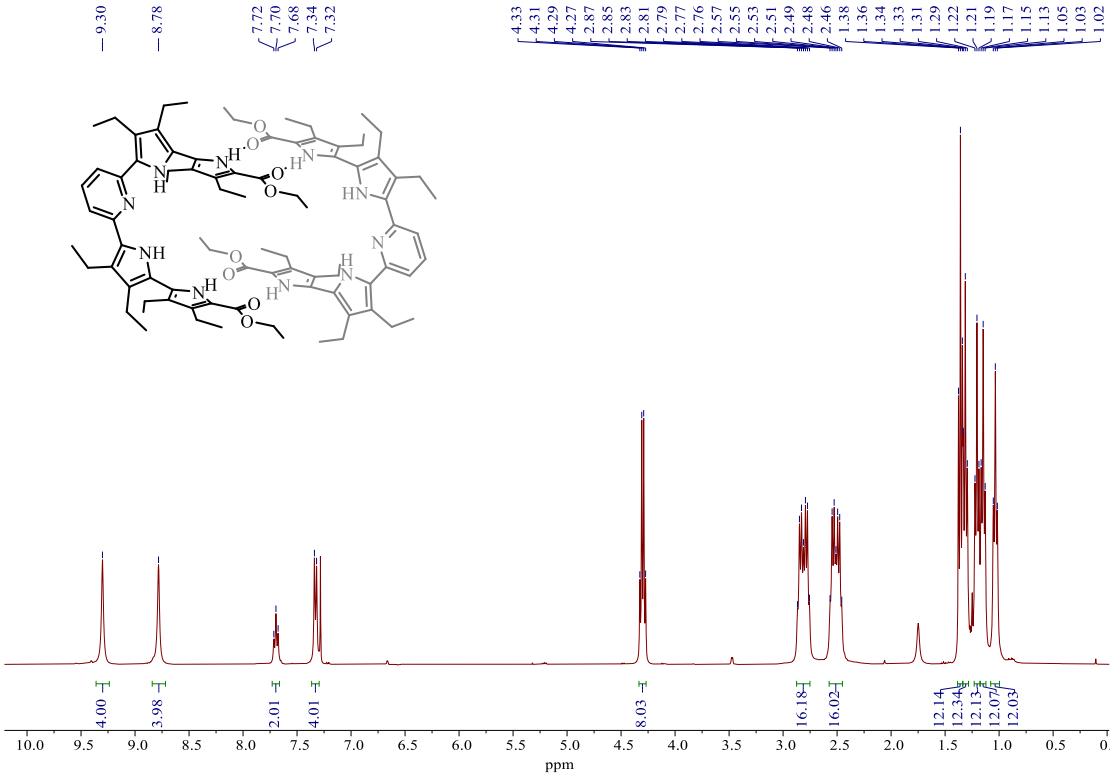


Figure S1. ^{1}H NMR spectrum of **2** recorded in chloroform-*d*.

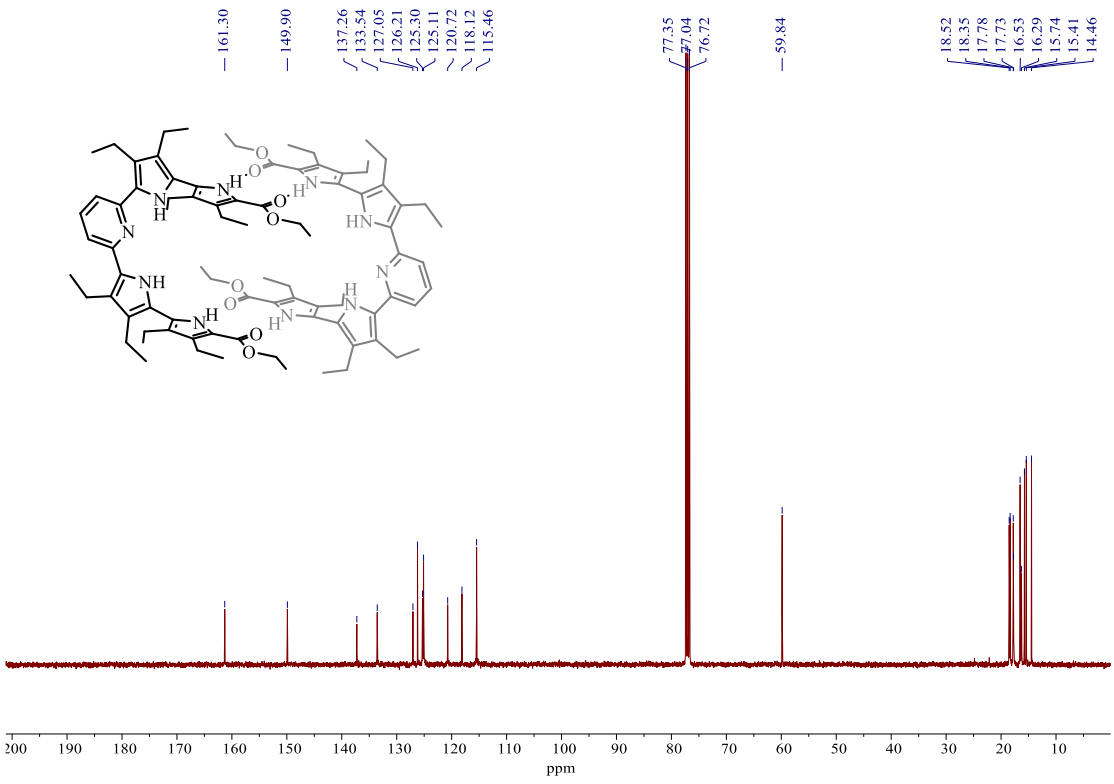


Figure S2. ^{13}C NMR spectrum of **2** recorded in chloroform-*d*.

3. MS spectra

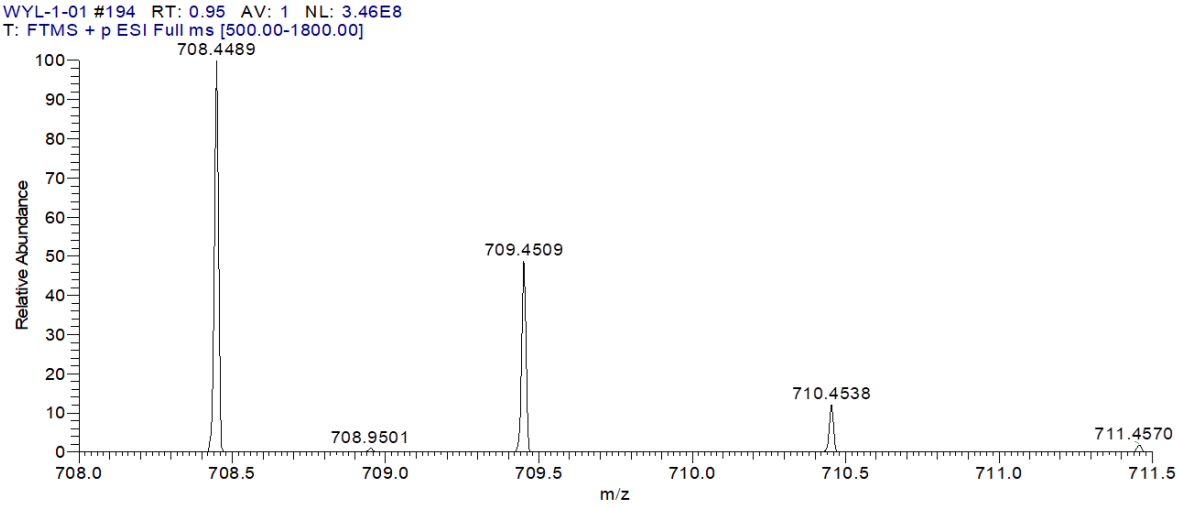


Figure S3. High resolution Mass spectrum of **2**.

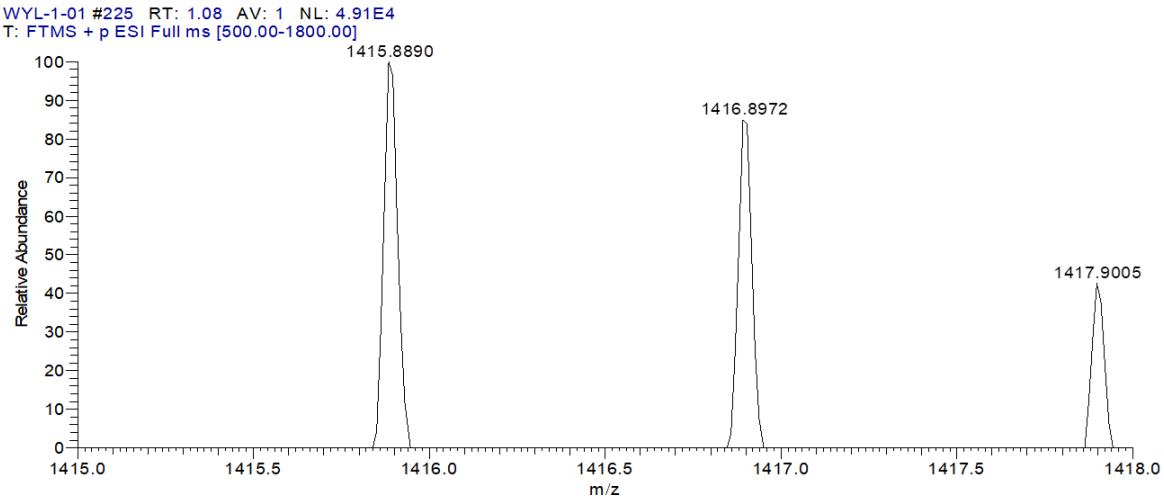


Figure S4. High resolution Mass spectrum of **2**·**2**.

4. DOSY NMR spectrum

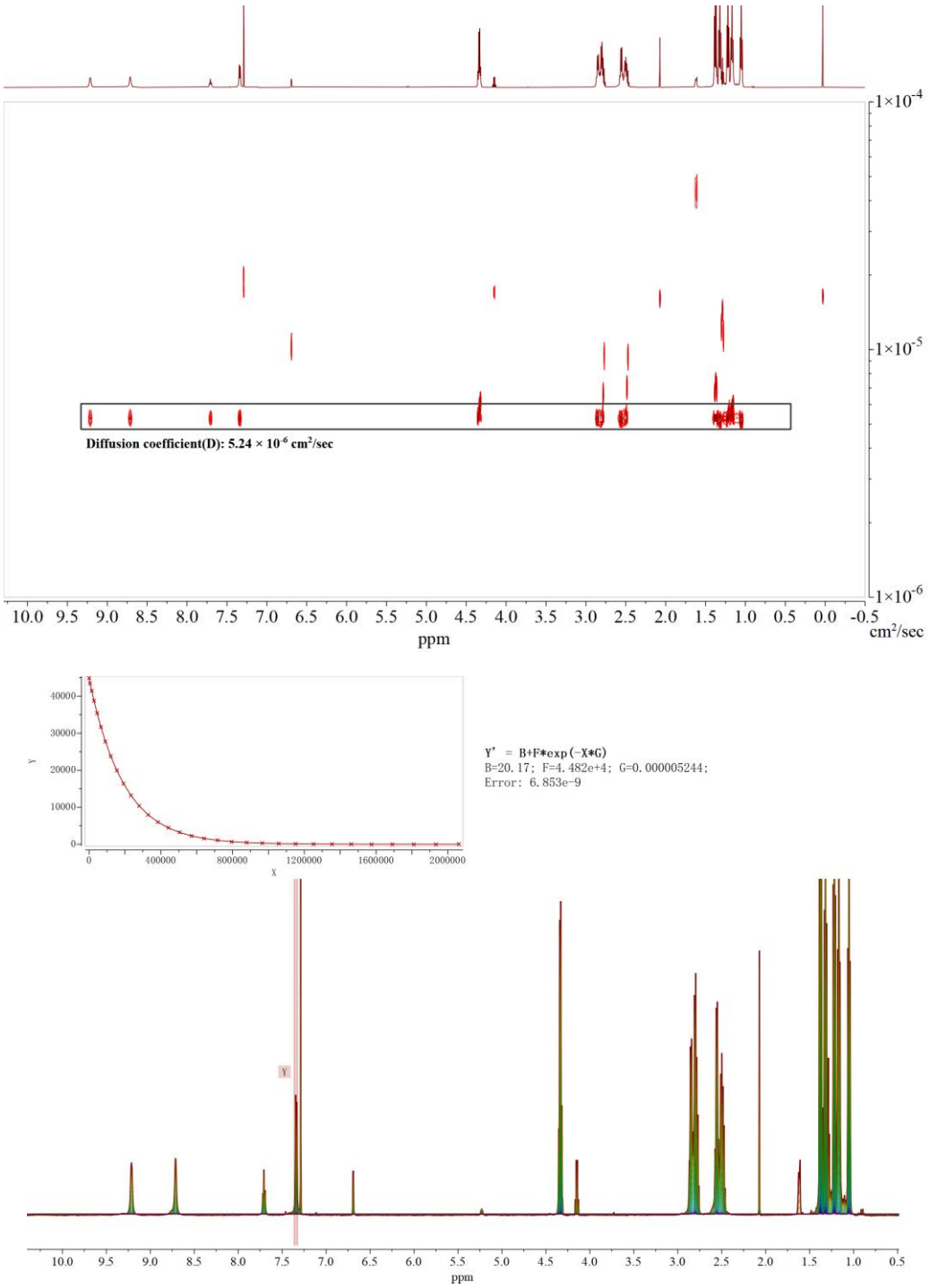


Figure S5. ^{1}H DOSY NMR spectrum of **2** recorded in chloroform-*d* (top) and fitting parameters (bottom).

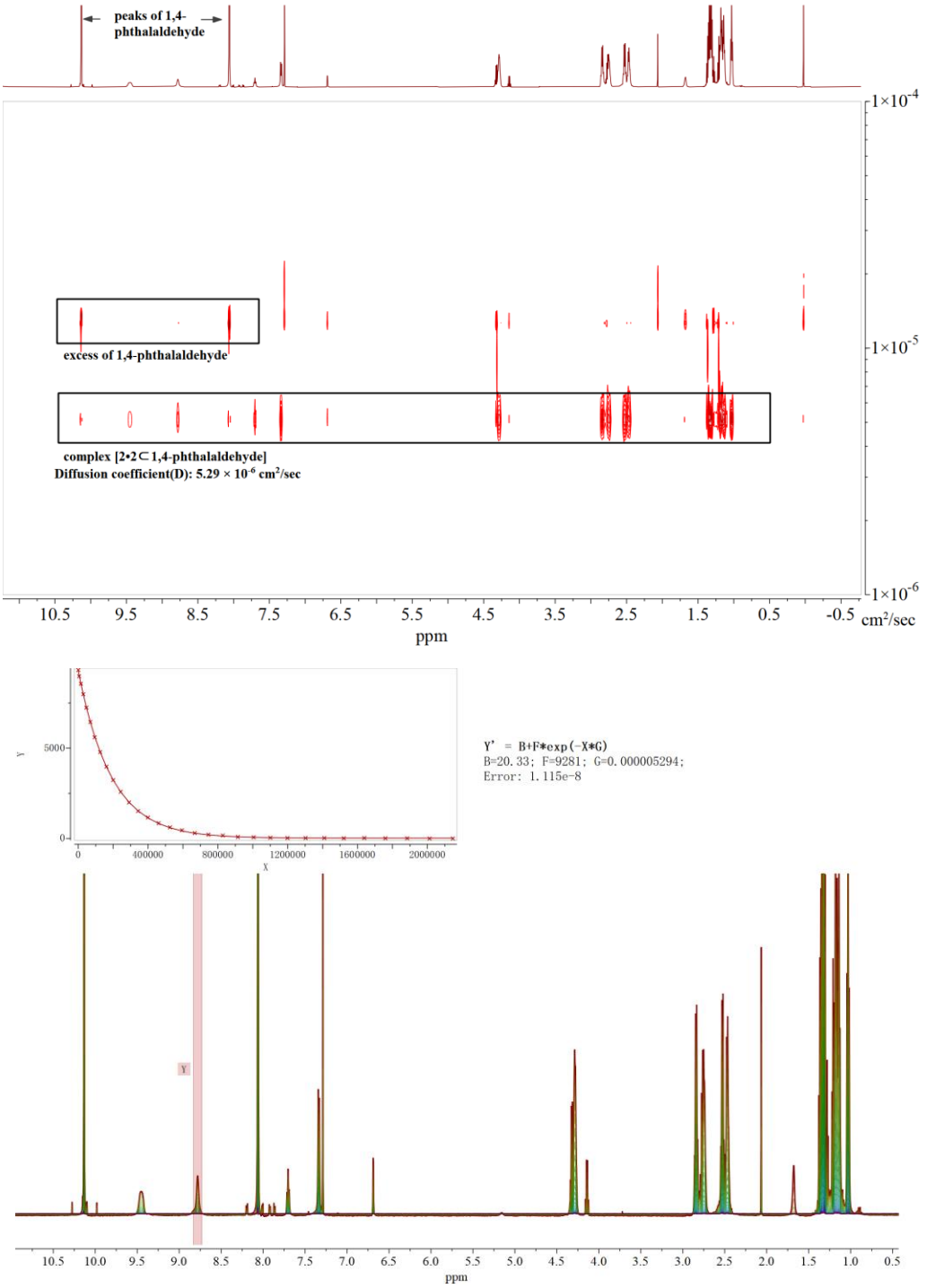


Figure S6. ^{1}H DOSY NMR spectrum of **2** in the presence of excess 1,4-phthalaldehyde recorded in chloroform-*d*(top) and fitting parameters (bottom) in the presence of excess 1,4-phthalaldehyde.

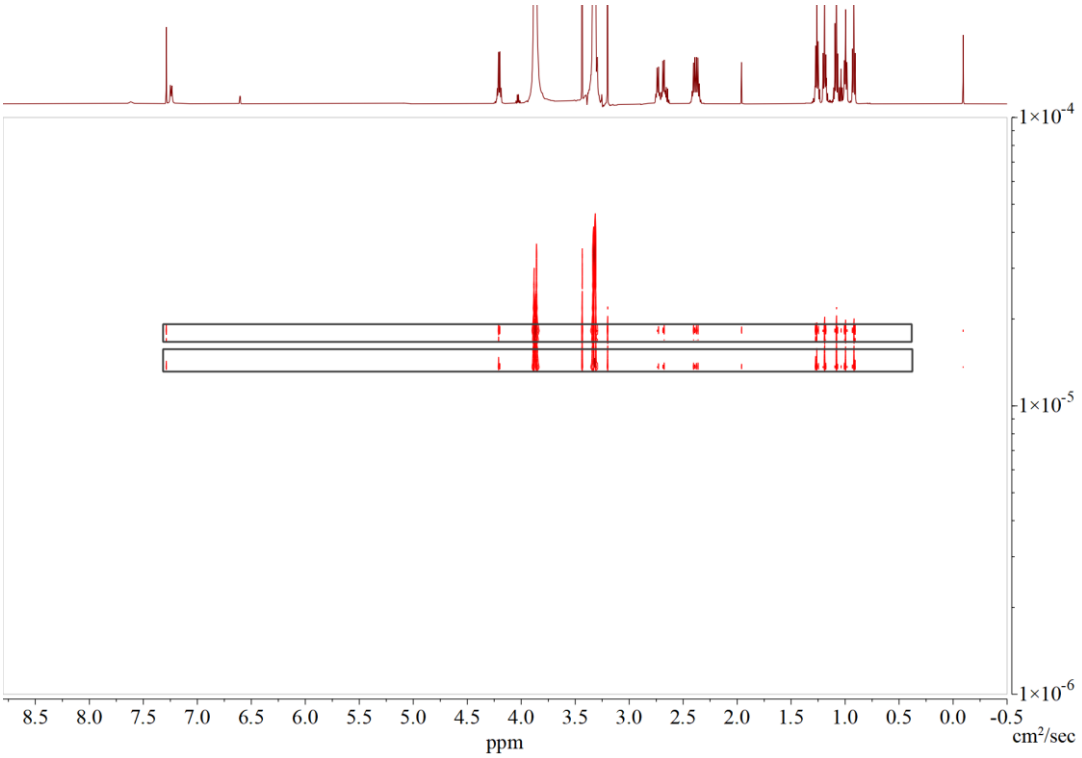


Figure S7. ^{1}H DOSY NMR spectrum of **2** in the presence of methanol recorded in chloroform-*d*.

5. NMR titrations.

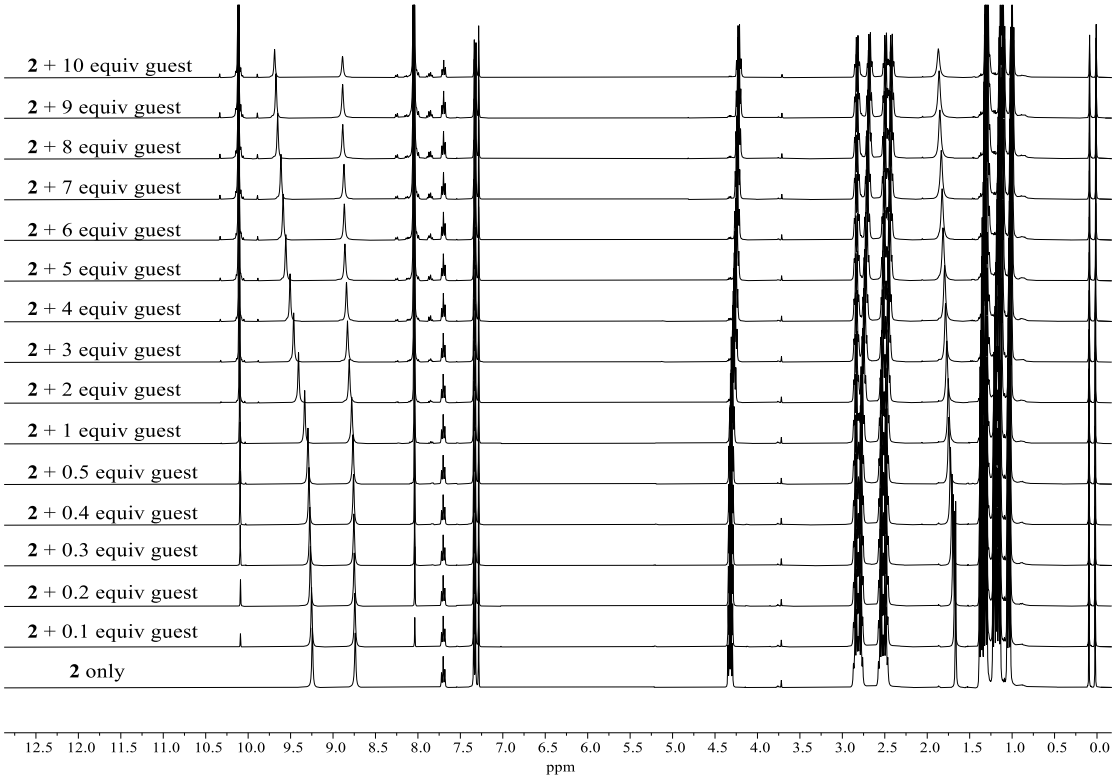


Figure S8. ^{1}H NMR spectra recorded during the titration of **2** with 1,4-phthalaldehyde in chloroform-*d*. Note: the binding constant was undeterminable.

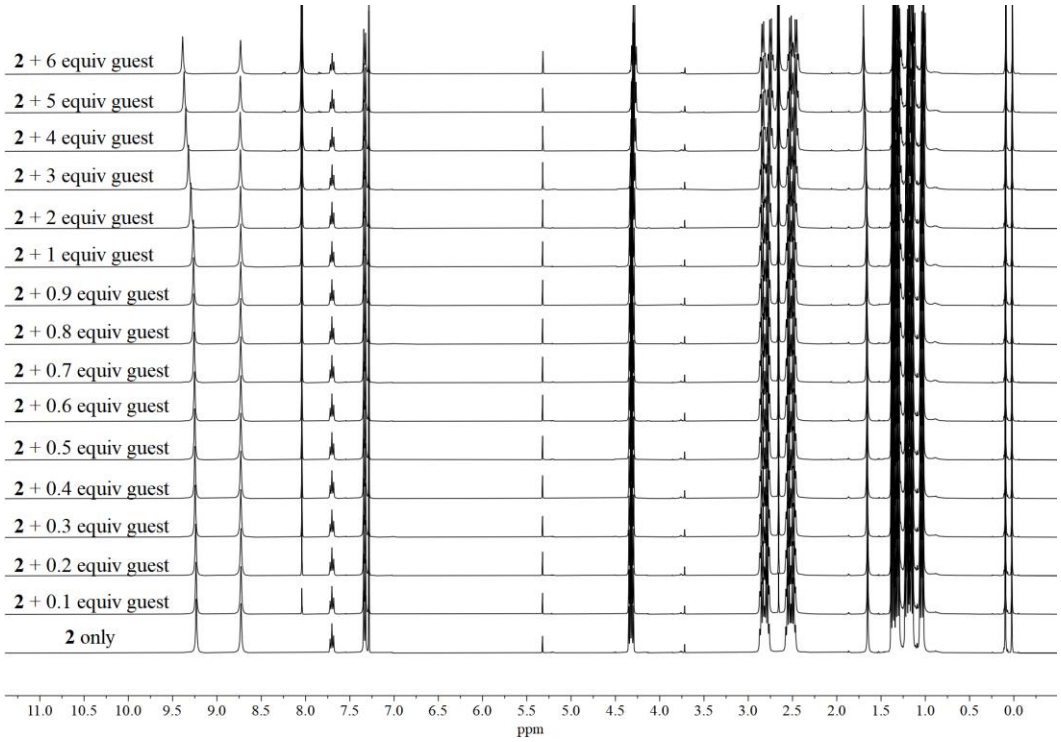


Figure S9. ^{1}H NMR spectra recorded during the titration of **2** with 1,4-diacetylbenzene in chloroform-*d*. Note: the binding constant was undeterminable.

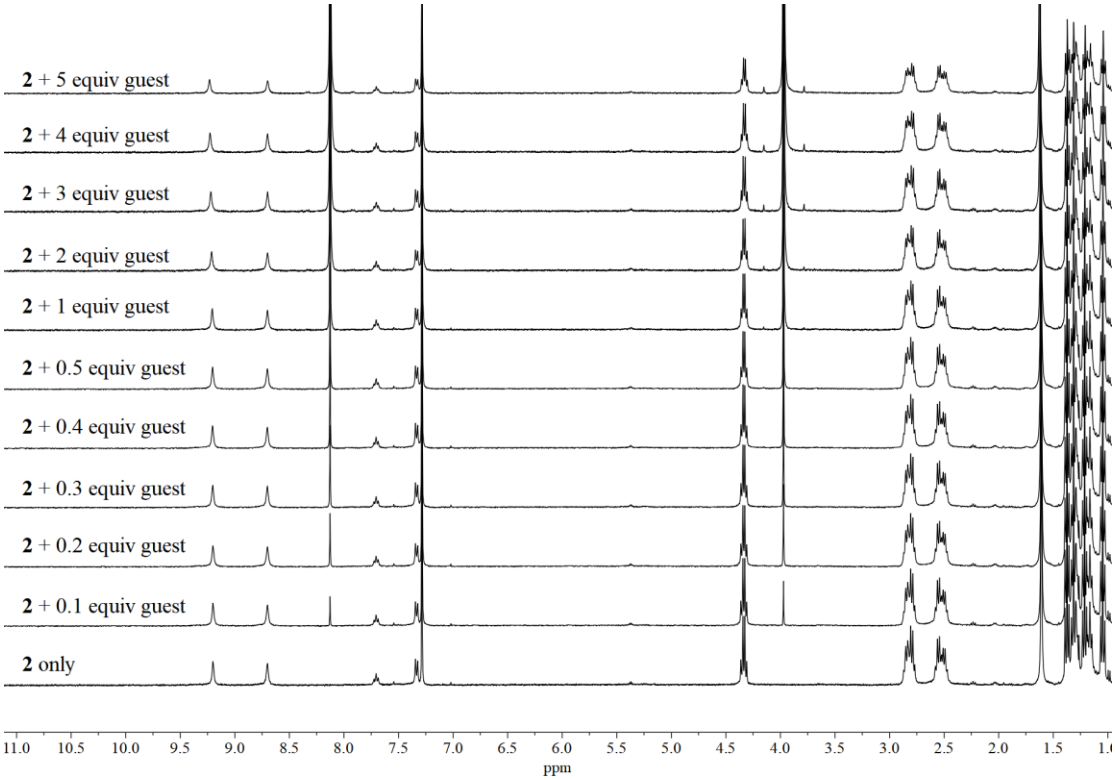


Figure S10. ^{1}H NMR spectra recorded during the titration of **2** with *p*-phthalate in chloroform-*d*. Note: the binding constant was undeterminable.

6. X-Ray experimental

[2•2⊂DCE] (CCDC No.: 2419260)

Crystals grew as colourless blocks upon the slow diffusion of a DCE/hexanes solution of **2**. The data crystal had approximate dimensions of 0.30 x 0.20 x 0.15 mm. All measurements were made on a Bruker Bruker Photon III 28 diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 100 K. Of the 47442 reflections that were collected, 10460 were unique (R_{int} = 0.0569). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S1. Crystal data for [2•2⊂DCE].

Empirical Formula		$C_{46}H_{63.5}Cl_{1.5}N_5O_4$
Formula Weight		803.69
Temperature		100 K
Crystal Color, Habit		colourless, block
Crystal Dimensions		0.30 X 0.20 X 0.15 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	12.6355(6)
	b/Å	14.5471(7)
	c/Å	15.0531(7)
	α/deg	61.623(2)
	β/deg	70.727(2)
	γ/deg	67.089(2)
	V/Å^3	2206.18(19)
Z Value		2
D_{calc}/g cm^{-3}		1.210
F_{000}		864
No. of Reflections Measured	Total:	47442
	Unique:	10460 (R_{int} = 0.0569)
Data/restraints/parameters		10460/13/596
R1; *wR2* (all data)		0.0637; 0.1526
Goodness of Fit Indicator (GOF)		1.057
R1; *wR2* (I>2σ(*I*))		0.0536; 0.1449

[2•2⊂(acetone)$_2$] (CCDC No.: 2419261)

Crystals grew as yellow blocks upon the slow diffusion of hexanes into an acetone solution of **2**. The data crystal had approximate dimensions of 0.2 x 0.1 x 0.1 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 200 K. Of the 27901 reflections that were collected, 8726 were unique (R_{int} = 0.0315). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S2. Crystal data for [2•2⊂(acetone)$_2$].

Empirical Formula		$C_{49}H_{69}N_5O_6$
Formula Weight		824.09
Temperature		200 K
Crystal Color, Habit		yellow, block
Crystal Dimensions		0.20 X 0.10 X 0.10 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	12.1297(6)
	b/Å	14.6354(7)
	c/Å	15.2121(7)
	α/deg	104.8440(10)
	β/deg	113.2370(10)
	γ/deg	90.513(2)
	V/Å^3	2380.1(2)
Z Value		2
D_{calc}/g cm^{-3}		1.150
F_{000}		892
No. of Reflections Measured	Total:	27901
	Unique:	8726 (R_{int} = 0.0315)
Data/restraints/parameters		8726/57/615
R1; *wR2* (all data)		0.0562; 0.1458
Goodness of Fit Indicator (GOF)		1.045
R1; *wR2* (I>2σ(*I*))		0.0515; 0.1409

[2•2⊂(MeOH)$_4$] (CCDC No.: 2419262)

Crystals grew as yellow blocks upon the slow diffusion of a DCM/methanol/hexanes solution of **2**. The data crystal had approximate dimensions of 0.12 x 0.10 x 0.10 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 100 K. Of the 62623 reflections that were collected, 20537 were unique (R_{int} = 0.0407). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S3. Crystal data for [2•2⊂(MeOH)$_4$].

Empirical Formula		$C_{92}H_{134}Cl_4N_{10}O_{12}$
Formula Weight		1713.88
Temperature		100 K
Crystal Color, Habit		yellow, block
Crystal Dimensions		0.12 X 0.10 X 0.10 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	15.1531(9)
	b/Å	17.6198(11)
	c/Å	19.7365(12)
	α/deg	104.8440(10)
	β/deg	90.793(2)
	γ/deg	113.600(2)
	V/Å^3	4677.8(5)
Z Value		2
D_{calc}/g cm^{-3}		1.217
F_{000}		1840
No. of Reflections Measured	Total:	62623
	Unique:	20537 (R_{int} = 0.0407)
Data/restraints/parameters		20537/27/1161
R1; *wR2* (all data)		0.0760; 0.1933
Goodness of Fit Indicator (GOF)		1.035
R1; *wR2* (I>2σ(*I*))		0.0727; 0.1909

[2•2⊂1,4-phthalaldehyde] (CCDC No.: 2419263)

Crystals grew as yellow blocks upon the slow diffusion of a DCM/hexanes solution of **2** and 1,4-phthalaldehyde. The data crystal had approximate dimensions of 0.3 x 0.2 x 0.2 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 200 K. Of the 43913 reflections that were collected, 9436 were unique (R_{int} = 0.0503). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S4. Crystal data for [2•2⊂1,4-phthalaldehyde].

Empirical Formula		$C_{47}H_{60}N_5O_5$
Formula Weight		775.00
Temperature		200 K
Crystal Color, Habit		yellow, block
Crystal Dimensions		0.30 X 0.20 X 0.20 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	12.8152(5)
	b/Å	14.8332(6)
	c/Å	14.9878(6)
	α/deg	96.2640(10)
	β/deg	111.7590(10)
	γ/deg	113.2860(10)
	V/Å^3	2318.80(16)
Z Value		2
D_{calc}/g cm^{-3}		1.110
F_{000}		834
No. of Reflections Measured	Total:	43913
	Unique:	9436 (R_{int} = 0.0503)
Data/restraints/parameters		9436/0/524
R1; *wR2* (all data)		0.0740; 0.1943
Goodness of Fit Indicator (GOF)		1.060
R1; *wR2* (I>2σ(*I*))		0.0592; 0.1792

[2•2⊂1,4-diacetylbenzene] (CCDC No.: 2419264)

Crystals grew as yellow blocks upon the slow diffusion of a DCM/hexanes solution of **2** and 1,4-diacetylbenzene. The data crystal had approximate dimensions of 0.3 x 0.2 x 0.2 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 200 K. Of the 53638 reflections that were collected, 10992 were unique (R_{int} = 0.0388). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S5. Crystal data for [2•2⊂1,4-diacetylbenzene].

Empirical Formula		$C_{48}H_{62}N_5O_5$
Formula Weight		789.02
Temperature		200 K
Crystal Color, Habit		yellow, block
Crystal Dimensions		0.30 X 0.20 X 0.20 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	12.1319(6)
	b/Å	14.3099(7)
	c/Å	15.1788(7)
	α/deg	102.7380(10)
	β/deg	110.4360(10)
	γ/deg	93.011(2)
	V/Å^3	2384.2(2)
Z Value		2
D_{calc}/g cm^{-3}		1.099
F_{000}		850
No. of Reflections Measured	Total:	53638
	Unique:	10992 (R_{int} = 0.0388)
Data/restraints/parameters		10992/95/677
R1; *wR2* (all data)		0.0741; 0.2143
Goodness of Fit Indicator (GOF)		1.072
R1; *wR2* (I>2σ(*I*))		0.0632; 0.1992

[2•2⊂ *p*-phthalate] (CCDC No.: 2419265)

Crystals grew as yellow blocks upon the slow diffusion of a DCM/hexanes solution of **2** and *p*-phthalate. The data crystal had approximate dimensions of 0.2 x 0.1 x 0.1 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 200 K. Of the 84213 reflections that were collected, 14266 were unique (R_{int} = 0.0345). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S6. Crystal data for [2•2⊂ *p*-phthalate].

Empirical Formula		$C_{48}H_{62}N_5O_6$
Formula Weight		805.02
Temperature		200 K
Crystal Color, Habit		yellow, block
Crystal Dimensions		0.20 X 0.10 X 0.10 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	12.1303(6)
	b/Å	14.6397(6)
	c/Å	15.2164(6)
	α/deg	104.2990(10)
	β/deg	111.8870(10)
	γ/deg	92.417(2)
	V/Å^3	2402.50(18)
Z Value		2
D_{calc}/g cm^{-3}		1.113
F_{000}		866
No. of Reflections Measured	Total:	84213
	Unique:	14266 (R_{int} = 0.0345)
Data/restraints/parameters		14266/23/631
R1; *wR2* (all data)		0.0599; 0.1795
Goodness of Fit Indicator (GOF)		1.040
R1; *wR2* (I>2σ(*I*))		0.0547; 0.1720

[2•2⊂TCBQ] (CCDC No.: 2419266)

Crystals grew as black blocks upon the slow diffusion of a DCM/hexanes solution of **2** and TCBQ. The data crystal had approximate dimensions of 0.12 x 0.10 x 0.10 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 200 K. Of the 105514 reflections that were collected, 18551 were unique (R_{int} = 0.0558). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S7. Crystal data for [2•2⊂TCBQ].

Empirical Formula		$C_{94}H_{118}Cl_8N_{10}O_{10}$
Formula Weight		1831.58
Temperature		200 K
Crystal Color, Habit		black, block
Crystal Dimensions		0.12 X 0.10 X 0.10 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	15.361(2)
	b/Å	17.925(3)
	c/Å	19.975(3)
	α/deg	103.894(5)
	β/deg	91.039(5)
	γ/deg	114.731(5)
	V/Å^3	4805.0(12)
Z Value		2
D_{calc}/g cm^{-3}		1.266
F_{000}		1936
No. of Reflections Measured	Total:	105514
	Unique:	18551 (R_{int} = 0.0558)
Data/restraints/parameters		18551/8/1140
R1; *wR2* (all data)		0.0873; 0.1977
Goodness of Fit Indicator (GOF)		1.082
R1; *wR2* (I>2σ(*I*))		0.0652; 0.1855

[2•2⊂BQ] (CCDC No.: 2419266)

Crystals grew as black blocks upon the slow diffusion of a DCM/hexanes solution of **2** and BQ. The data crystal had approximate dimensions of 0.12 x 0.10 x 0.06 mm. All measurements were made on a Bruker D8 diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 100 K. Of the 96441 reflections that were collected, 15527 were unique (R_{int} = 0.0853). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S7. Crystal data for [2•2⊂TCBQ].

Empirical Formula		$C_{98}H_{131}N_{10}O_{10}$
Formula Weight		1609.12
Temperature		100 K
Crystal Color, Habit		black, block
Crystal Dimensions		0.12 X 0.10 X 0.06 mm
Crystal System		Triclinic
Space Group		*P-1*
Lattice Parameters	*a*/Å	14.8218(17)
	b/Å	15.0041(18)
	c/Å	24.178(3)
	α/deg	99.601(6)
	β/deg	94.150(5)
	γ/deg	118.184(5)
	V/Å^3	4601.7(10)
Z Value		2
D_{calc}/g cm^{-3}		1.161
F_{000}		1738
No. of Reflections Measured	Total:	96441
	Unique:	15527 (R_{int} = 0.0853)
Data/restraints/parameters		15527/61/1113
R1; *wR2* (all data)		0.1634; 0.3616
Goodness of Fit Indicator (GOF)		1.070
R1; *wR2* (I>2σ(*I*))		0.1456; 0.3490

[2•2⊂1,4-dicaynobenzene] (CCDC No.: 2419267)

Crystals grew as colourless blocks upon the slow diffusion of a DCM/hexanes solution of **2** and 1,4-dicaynobenzene. The data crystal had approximate dimensions of 0.15 x 0.12 x 0.10 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 200 K. Of the 27051 reflections that were collected, 5675 were unique (R_{int} = 0.0372). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

Table S8. Crystal data for [2•2⊂1,4-dicaynobenzene].

Empirical Formula		$C_{47}H_{59}N_6O_4$
Formula Weight		772.00
Temperature		200 K
Crystal Color, Habit		colourless, block
Crystal Dimensions		0.15 X 0.12 X 0.10 mm
Crystal System		Monoclinic
Space Group		*C2/m*
Lattice Parameters	*a*/Å	13.5541(10)
	b/Å	25.3522(19)
	c/Å	15.2379(11)
	α/deg	90
	β/deg	104.797(3)
	γ/deg	90
	V/Å^3	5062.5(6)
Z Value		4
D_{calc}/g cm^{-3}		1.013
F_{000}		1660
No. of Reflections Measured	Total:	27051
	Unique:	5675 (R_{int} = 0.0372)
Data/restraints/parameters		5675/0/280
R1; *wR2* (all data)		0.0539; 0.1473
Goodness of Fit Indicator (GOF)		1.095
R1; *wR2* (I>2σ(*I*))		0.0468; 0.1473