Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Solvent-induced reversible solid-state colour change of an intramolecular charge-transfer complex

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Additional Figures and Tables.

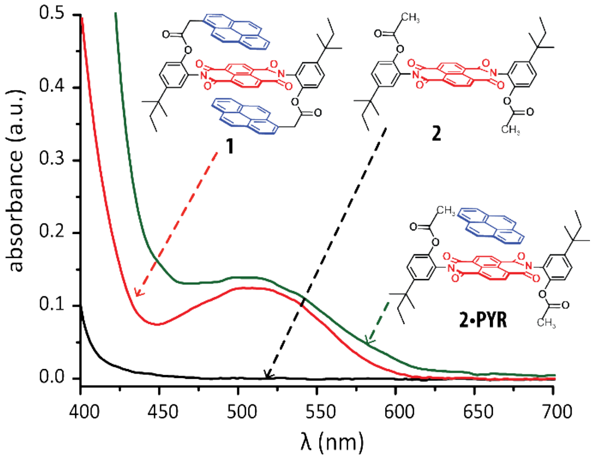


Figure S1 UV-vis spectra of molecular CT model **1** (red trace) and control **2** (black trace) at 0.25 mM in chloroform and the intermolecular **2**•PYR complex (green trace) at 6.55 mM in chloroform.

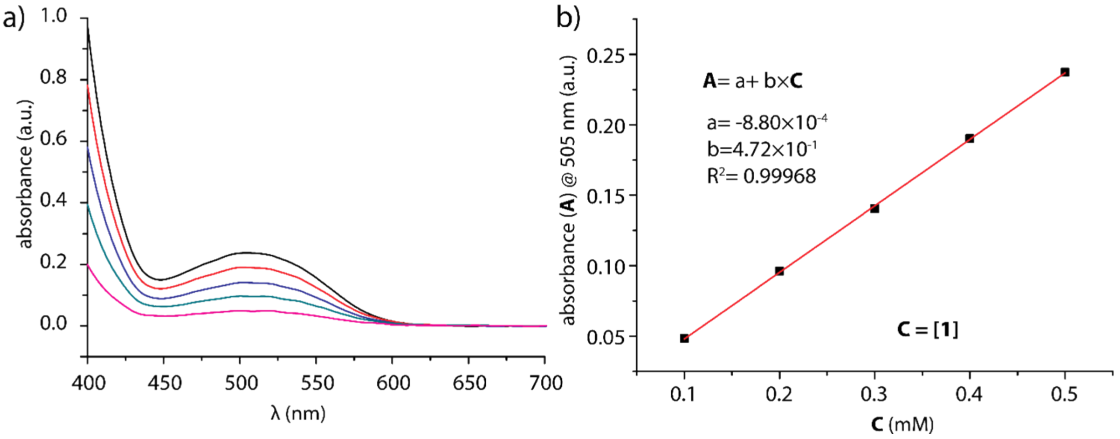


Figure S2. Partial UV/vis spectra of **1** in chloroform from 0.1 to 0.5 mM highlighting the charge-transfer absorption band (left), and the linear fitting of absorption (**A**) at λ_{max} = 505 nm against the concentration of **1** (right).

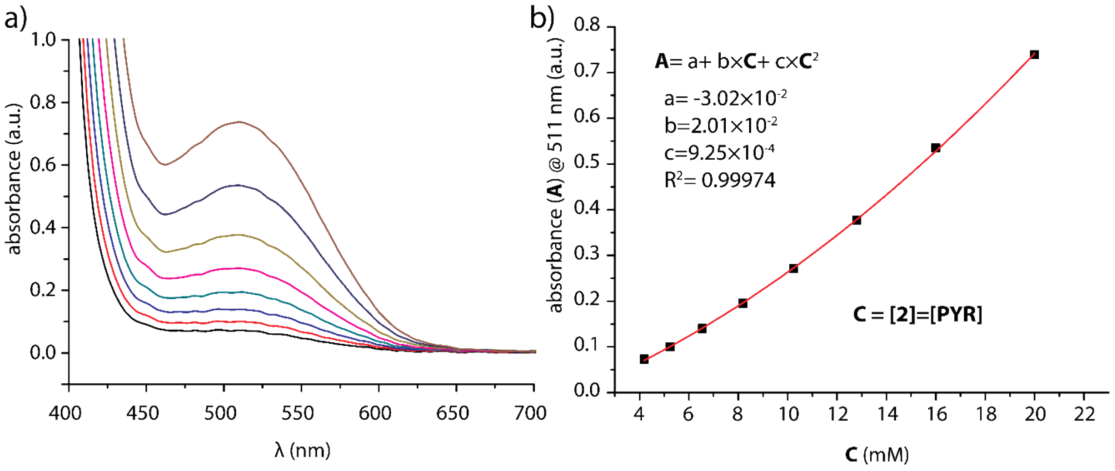


Figure S3 Partial UV/vis spectra of **2·PYR** in chloroform from 4.2 to 20 mM highlighting the charge-transfer absorption band (left), and the polynomial fitting of absorption (**A**) at λ_{max} = 511 nm against the concentration of **[2]** (right).

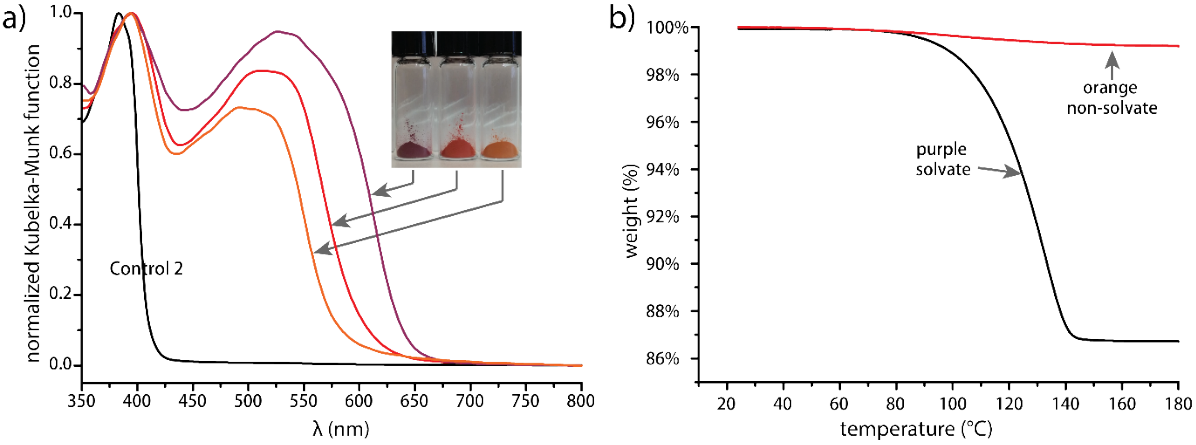


Figure S4 (a) Normalized solid-state diffuse reflectance UV-vis spectra for purple and red solid of **1** (inlet) and white solid of control **2**; (b) TGA traces of the purple (black) and orange (red) powders of **1**.

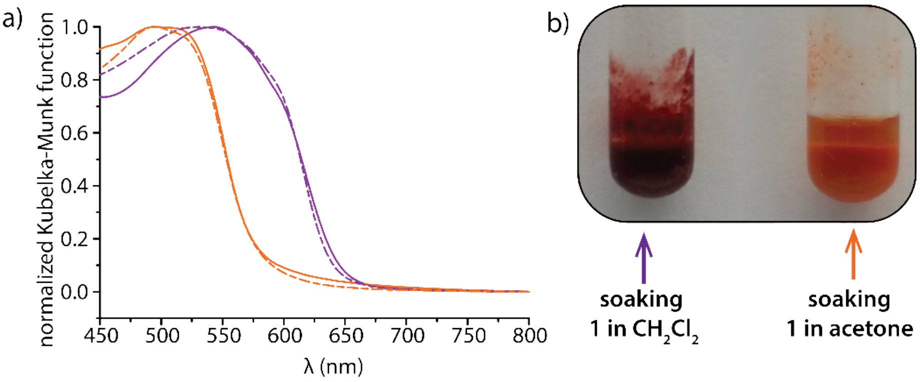


Figure S5. (a) Solid-state diffuse reflectance UV-vis spectra of purple and orange solids (coloured solid traces) and dichloromethane-solvate and non-solvate crystals (coloured dashed traces) of **1**, highlighting the similarity in colour between the solid and crystal samples. (b) Soaking **1** in a minimum amount of dichloromethane and acetone, highlighting the sensitivity of colour change.

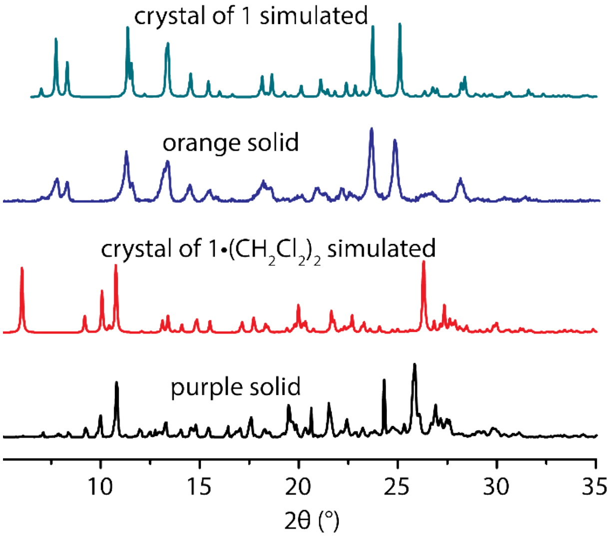


Figure S6. Powder X-ray diffraction data for the orange and purple solids of **1** together with the simulated powder patterns from the crystal structures **1** and **1**•$(CH_2Cl_2)_2$.

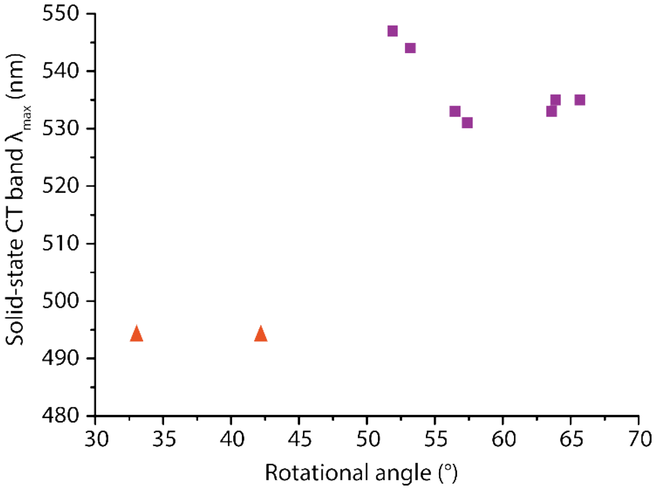


Figure S7 Scatter plot of the CT band λ_{max} against the rotational angle (***θ***) between PYR and NDI units of the intramolecular CT complexes in the six crystal structures of **1**, highlighting the ***θ*** angle difference between the solvate (■) and non-solvate structures (▲).

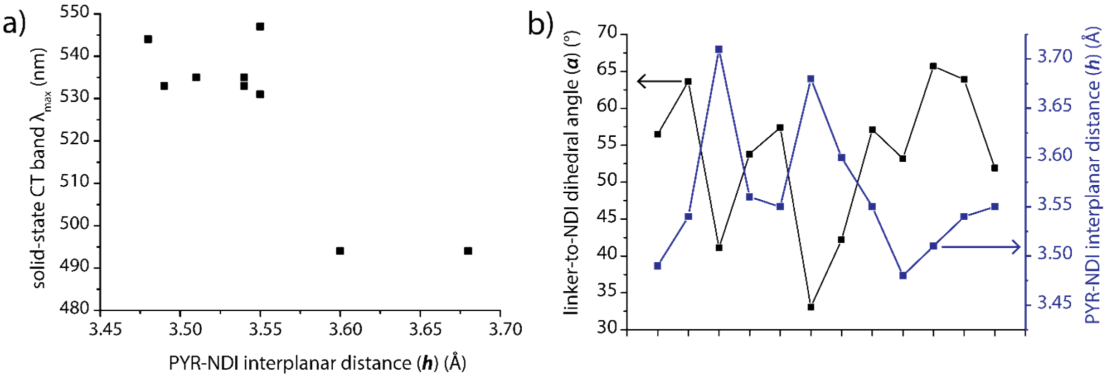
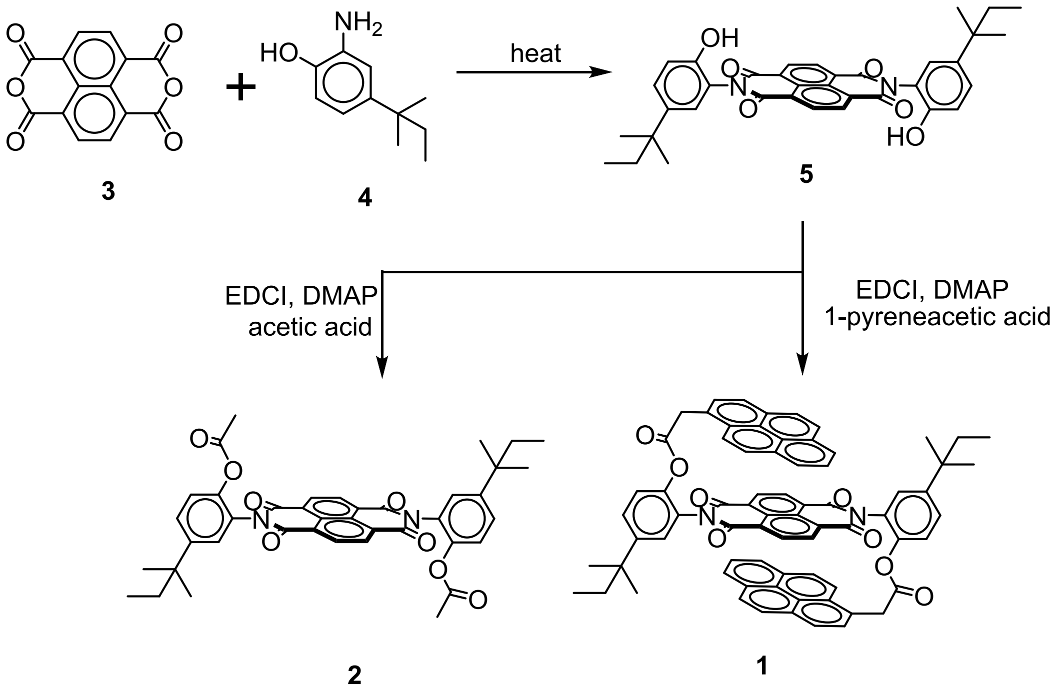


Figure S8 (a) Scatter plot of the CT band λ_{max} against the PYR-NDI interplanar distance (***h***) of the intramolecular CT complexes in the six crystal structures of **1**, highlighting their *insignificant* correlation due to the small difference in ***h*** (~0.05 Å) between the solvate and non-solvate structures. (b) Double-Y plot of the linker-to-NDI dihedral angle (***α***) and PYR-NDI interplanar distance (***h***) of the intramolecular CT complexes in the six crystal structures, highlighting that variations in the PYR-NDI interplanar distance were tightly related to the linker rotation. All observed conformations were included. Definitions of geometric parameters ***α*** and ***h*** are illustrated in Figure S9.

Synthesis and Characterization.

General Experimental. All chemicals were purchased from commercial suppliers and used as received unless otherwise noted. All reactions were carried out under a dry N_2 atmosphere in oven–dried glassware. Dry organic solvents were obtained by passing the degassed solvents through activated alumina columns. Flash chromatography was carried out using either silica gel (60 Å, 200–400 mesh). Thin layer chromatography (TLC) for monitoring the reaction progress was performed using either precoated 0.25 mm silica gel 60 F254 plates. NMR spectra were recorded on 300 MHz, 400 MHz spectrometers. Chemical shifts are reported in ppm (δ) referenced to TMS. HRMS was recorded with a magnetic sector spectrometer using EI sources and the Q-TOF 1 spectrometer using ESI sources.

Scheme S1. Syntheses of molecular sensor **1** and control **2**



Bisphenol **5** was obtained as previous reported;[1] thermal condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride (**3**) and 2-amino-4-*tert*-amylphenol (**4**). The esterification of 1-pyreneacetic acid and bisphenol **5** using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and *N, N*-dimethylaminopyridine (DMAP) in acetonitrile at room temperature gave the crude product **1** that consisted of both *anti* and *syn* conformers. The crude **1** was then thermally equilibrated at 80 ºC

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[1] Chong, Y. S.; Carroll, W. R.; Burns, W. G.; Smith, M. D.; Shimizu, K. D. *Chem.-Eur. J.* **2009**, *15*, 9117.

for 10 h in 1,1,2,2-tetrachloroethane (TCE) and precipitated in CH_2Cl_2/acetonitrile giving the pure *anti* conformer of **1** as purple colour powder. Control **2** was obtained similarly from bisphenol **5** and acetic acid as a white powder. Thermal equilibration of **2** gave a mixture of approximately 1:1 *anti* and *syn* conformers. Molecular models **1** and control **2** are newly reported compounds, and their ^1H and ^{13}C spectra are provided.

(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis(4-(*tert*-pentyl)-2,1-phenylene) bis(2-(pyren-1-yl)acetate). (**1**) Bisphenol **5** (100 mg, 0.17 mmol) was dissolved in 5 mL of dried acetonitrile. To the above solution, 1-pyreneacetic acid (130 mg, 0.51 mmol), DMAP (10 mg, 0.09 mmol) and EDCI (80 mg, 0.51 mmol) were added. The reaction mixture was stirred at room temperature for 12 h, and the solvent was then removed under vacuum. The residue was dissolved in dichloromethane (40 mL), washed with water (2×40 mL), sodium carbonate solution (2×40 mL), and brine (40 mL), and dried with $MgSO_4$. The solvent was removed in vacuum, and solid residue was suspended in acetone. The orange insoluble was collected by filtration as crude 1 (130 mg, 71 %). Crude **1** was dissolved in TCE (5 mL) and heated at 80 C under N_2 for 10 h to equilibrate. The solvent was removed under vacuum giving a purple solid residue, which upon recrystallization in CH_2Cl_2/AcCN gave pure anti conformer of **1** as a purple solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 9.2$ Hz, 2H), 7.76 – 7.27 (m, 20H), 6.95 (s, 4H), 4.22 (s, 4H), 1.84 (q, $J = 7.5$ Hz, 4H), 1.50 (s, 12H), 0.93 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (100 MHz, TCE-d_2) δ 167.95, 160.83, 148.37, 143.95, 129.74, 129.35, 129.16, 128.22, 128.06, 127.77, 127.38, 126.95, 126.79, 126.60, 125.87, 125.66, 125.54, 125.09, 124.75, 124.25, 123.30, 123.21, 123.14, 123.13, 122.73, 122.62, 77.43, 77.31, 77.11, 76.79, 39.80, 37.91, 36.94, 29.60, 28.43, 9.27. HRMS (ESI) m/z calcd for $[C_{72}H_{54}N_2O_8]^+$ (M^+): 1075.3958; found 1075.3925.

(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis(4-(*tert*-pentyl)-2,1-phenylene) diacetate. (**2**) Control **2** was synthesized using the same procedure described for **1** using bisphenol **5** (0.30 g, 0.51 mmol), acetic acid (87 µL, 1.52 mmol), DMAP (30 mg, 0.25 mmol) and EDCI (0.24 g, 1.52 mmol). Crude **2** was obtained as a white powder (0.25 g, 73%). Thermal equilibration in TCE at 80 °C under N_2 for 10 h gave a mixture of *anti* and *syn* conformers (1.2:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 4H syn and anti), 7.51 (dd, $J = 8.7$ Hz, $J = 2.3$ Hz, 2H syn and anti), 7.38 (d, $J = 8.7$ Hz, 2H anti), 7.37 (d, $J = 8.7$ Hz, 2H syn), 7.32 (d, $J = 2.3$ Hz, 2H anti), 7.29 (d, *J* = 2.3 Hz, 2H syn), 2.06 (s, 4H syn), 2.04 (s, 4H anti), 1.68 (q, *J* = 7.1 Hz, 4H syn), 1.67 (q, *J* = 7.1 Hz, 4H anti), 1.33 (s, 12H syn), 1.33 (s, 12H anti), 0.78 (t, *J* = 7.4 Hz, 6H syn and anti). ^{13}C NMR (100 MHz, TCE-d$_2$) δ 167.99, 167.94, 161.96, 148.11, 143.88, 131.44, 127.66, 127.34, 127.16, 127.08, 126.61, 126.58, 125.27, 125.17, 122.65, 37.72, 36.78, 28.14, 20.96, 20.81, 9.11. HRMS (ESI) m/z calcd for $[C_{40}H_{38}N_2O_8]^+$ (M^+): 674.2628; found: 674.2618.

Solvate and non-solvate single crystals of 1.

Five solvate and one non-solvate forms of single crystals of **1** were obtained through slow evaporation from organic solvents. Their resolved crystal structures were summarized as below.

One solvate single crystal was obtained from CH_2Cl_2 solution, and was found to have an empirical formula of $C_{74}H_{54}N_2O_8$•$2CH_2Cl_2$. Solvate **1**•$2CH_2Cl_2$ was an intense red plate crystal, in which $C_{74}H_{54}N_2O_8$ molecule (**1**) crystallized in the monoclinic space group $P2_1/n$. The asymmetric unit consist of half of $C_{74}H_{54}N_2O_8$ molecule and one dichloromethane molecule. The pyrene unit was found to disorder over two closely spaced, co-planar orientations via a *ca.* 12.5° 'pivot' around the ipso carbon. The population was refined to two conformations of 0.76/0.24 ratio. Disorder was also found for the inclusion dichloromethane over two positions. Repeating crystallization in CH_2Cl_2 gave the same crystal.

One solvate single crystal was obtained from the CH_2Cl_2/AcCN system, and was found to have an empirical formula of $C_{74}H_{54}N_2O_8$•1.36(CH_3CN)0.64(CH_2Cl_2). Solvate **1**•2(CH_3CN/CH_2Cl_2) was a dark red blocklike crystal in which $C_{74}H_{54}N_2O_8$ (**1**) crystallized in the monoclinic space group $P2_1/n$. The asymmetric unit consists of half of $C_{74}H_{54}N_2O_8$ molecule, which is located on an inversion center, and a volume of disordered solvent, which are CH_3CN and CH_2Cl_2. The solvent disorder was modeled with three independent groups: one acetonitrile and two dichloromethane groups. A slight positional disorder exist at the far end of pyrene units as suggested by the elongated displacement ellipsoids. A reasonable refinement, however, was achieved giving an average position for the pyrene unit (See later Crystal Structure Characterization section for detail). Disorder was also found at the *tert*-amyl group.

One non-solvate form of small crystal[2] was obtained from the $CHCl_3$/CH_3CN system, and was found to have an empirical formula of $C_{74}H_{54}N_2O_8$. Non-solvate **1** was a *thin yellow-orange plate* in which $C_{74}H_{54}N_2O_8$ (**1**) crystallized in the triclinic space group *P*-1. The asymmetric unit consists of half of $C_{74}H_{54}N_2O_8$ molecule, which is located on an inversion center. The disorder primarily takes the form of differently orientated but essentially co-planar pyrene motifs. The population fraction of each orientation was refined to be 0.72/0.28. The *tert*-amyl groups were also found to be disordered. No inclusion solvent molecules were found. Repeating crystallization in the $CHCl_3$/CH_3CN system

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[2] The data for structure resolution was instead collected using synchrotron at the X-ray crystallography facility at the Department of Chemistry, University of Cincinnati, Cincinnati, OH.

failed in obtaining good quality single crystals. Recrystallization in acetone, however, gave quality single crystals of the same non-sovlate **1** but with greater dimensions.

One solvate form of crystal was obtained from the CH_3NO_2, and was found to have an empirical formula of $C_{74}H_{54}N_2O_8 \bullet 2(CH_3NO_2)$. Solvate **1**$\bullet 2(CH_3NO_2)$ was a red plate crystal in which $C_{74}H_{54}N_2O_8$ (**1**) crystallized in the triclinic space group *P*-1. The asymmetric unit consists of half of $C_{74}H_{54}N_2O_8$ molecule, which is located on an inversion center, and one CH_3NO_2. No disorder was found. Repeating crystallization in CH_3NO_2 gave the same crystal.

One solvate form of crystal was obtained from the nitroethane, and was found to have an empirical formula of $C_{74}H_{54}N_2O_8 \bullet 2(CH_3CH_2NO_2)$. Solvate **1**$\bullet 2(CH_3CH_2NO_2)$ was a dark red tablet crystal in which $C_{74}H_{54}N_2O_8$ (**1**) crystallized in the triclinic space group *P*-1. The asymmetric unit consists of half each of two crystallographically independent $C_{74}H_{54}N_2O_8$ molecules, each of which is located on an inversion center, and two independent nitroethane molecules. The *tert*-amyl groups of each $C_{74}H_{54}N_2O_8$ molecule were found to be rotationally disordered. Repeating crystallization in the $EtNO_2$ system gave the same crystal.

One solvate form of crystal was obtained from the dioxane, and was found to have an empirical formula of $C_{74}H_{54}N_2O_8 \bullet 2(C_4H_8O_2)$. Solvate **1**$\bullet 2(C_4H_8O_2)$ was a thin red plate crystal in which $C_{74}H_{54}N_2O_8$ (**1**) crystallized in the monoclinic space group $P2_1/c$. The asymmetric unit consists of half of $C_{74}H_{54}N_2O_8$ molecule, which is located on an inversion centers, and one dioxane molecule. No disorder was found. Repeating crystallization in the dioxane system gave the same crystal.

One non-solvate crystal of **2** was obtain from chloroform, and was found to have an empirical formula of $C_{40}H_{38}N_2O_8$. Non-solvate **2** was a colourless tablet in which $C_{40}H_{38}N_2O_8$ (**2**) crystallized in the monoclinic space group $P2_1/c$. The asymmetric unit consists of half of $C_{40}H_{38}N_2O_8$ molecule, which is located on a crystallographic inversion center. No disorder was found. Repeating crystallization in chloroform gave the same crystal.

To effectively characterize and analyze these crystal structures and intramolecular PYR-NDI CT complex therein, several parameters were defined and measured (Figure S5). To characterize the length of the five-atom covalent linker, the distance (***l***) between carbonyl α-C and C_{aryl}-N_{imide} bond was measured. To characterize the conformational flexibility of the covalent linker, the dihedral angle ($\boldsymbol{\alpha}$) between phenyl ring and naphthalenediimide residing planes was measured. To characterize the rotational displacement between PYR and NDI units in the intramolecular CT complex, the rotational angle (***θ***) between their long axes was measured. To characterize the intramolecular aromatic stacking interaction between PYR and NDI units, the stacking angle (***β***) as defined by the dihedral angle of the PYR and NDI residing planes, the interplanar distance (***h***) as defined by the PYR centroid to NDI residing plane distance, and the horizontal displacement (***d***) as defined by the distance between the PYR centroid project and NDI centroid were measured. The measured values are provided in Table S1. The solid-state UV-vis spectra of these six single crystals are provided in Figure S10.

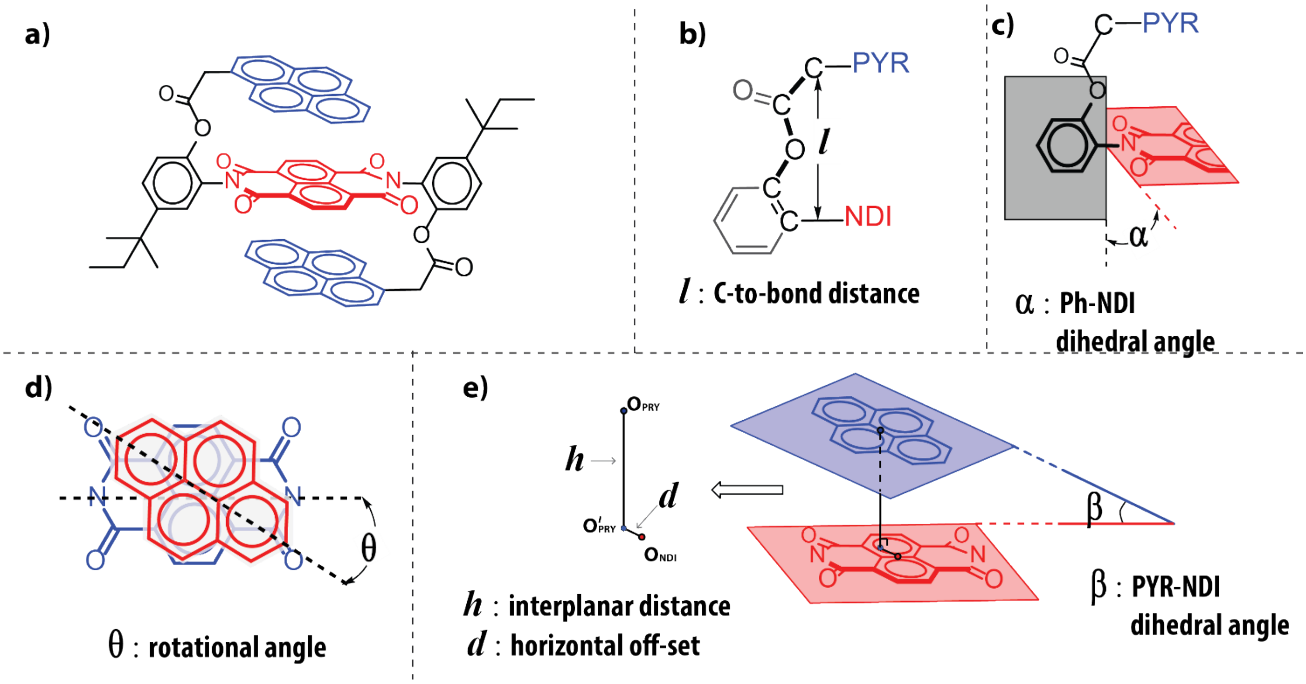

Figure S9. Geometric parameters defined to characterize the intramolecular PYR-NDI CT complex in **1**: (a) Chemdraw representation of **1** in side view; (b) the C-to-CN bond distance (***l***) for characterizing linker length; (c) the dihedral angle (***α***) between the N-Ph and NDI residing planes for characterizing the conformational flexibility of linker motif; (d) the twist angle (***θ***) defined by the long axes of PYR and NDI units; (e) the interplanar distance (***h***) between the PYR and NDI residing planes, the horizontal off-set (***d***) between the centroids of PYR and NDI units, and PYR-NDI stacking angle (***β***) for characterizing the intramolecular aromatic stacking interaction.

Table S 1. Measured geometric parameters in crystal structures of **1** and **2**

	inclusion solvent	solvent-to-**1** ratios	relative population[a]	rotation angle ($\boldsymbol{\theta}$)	dihedral angle ($\boldsymbol{\alpha}$)	interplanar distance ($\boldsymbol{h}$)	linker length ($\boldsymbol{l}$)	horizontal offset ($\boldsymbol{d}$)	stacking angle ($\boldsymbol{\beta}$)	CT profile[e]		
										λ_{max} (nm)	$\lambda_{half\text{-}height}$ (nm)	$\lambda_{on\text{-}set}$ (nm)
1	CH_2Cl_2	2:1	76%[b]	56.5	78.4	3.49	4.48	0.17	6.3	533	613	638
			24%[b]	63.6	78.4	3.54	4.48	0.57	7.1			
	CH_2Cl_2 & CH_3CN[d]	2:1	100%	57.4	76.9	3.55	4.48	0.25	6.4	531	620	646
	none	0	28%[b]	33.1	75.4	3.68	4.41	0.58	5.1	494	553	578
			72%[b]	42.2	75.4	3.60	4.36	0.35	5.7			
	CH_3NO_2	2:1	100%	53.2	83.5	3.48	4.43	0.19	5.6	544	629	658
	$EtNO_2$	2:1	50%[c]	65.7	74.6	3.51	4.49	0.80	7.4	535	612	643
			50%[c]	63.9	72.2	3.54	4.51	0.55	7.4			
	dioxane	2:1	100%	51.9	73.8	3.55	4.50	0.38	4.7	547	591	612
2	none	0	100%	n/a	89.5	n/a	4.64	n/a	n/a	n/a	n/a	n/a

[a] Relative population of multiple PYR-NDI geometries from partial disorder or multiple crystallographically independent molecules. (See later structure analysis section for details); [b] Partial disorder at the pyrene motif was resolved into two slightly differently CT interaction geometries; [c] Two crystallographically independent molecules of **1** were observed; [d] A volume of disordered solvent was modeled into three independent groups: one acetonitrile and two dichloromethane groups. [e] The UV-vis spectra were provided in Figure S10.

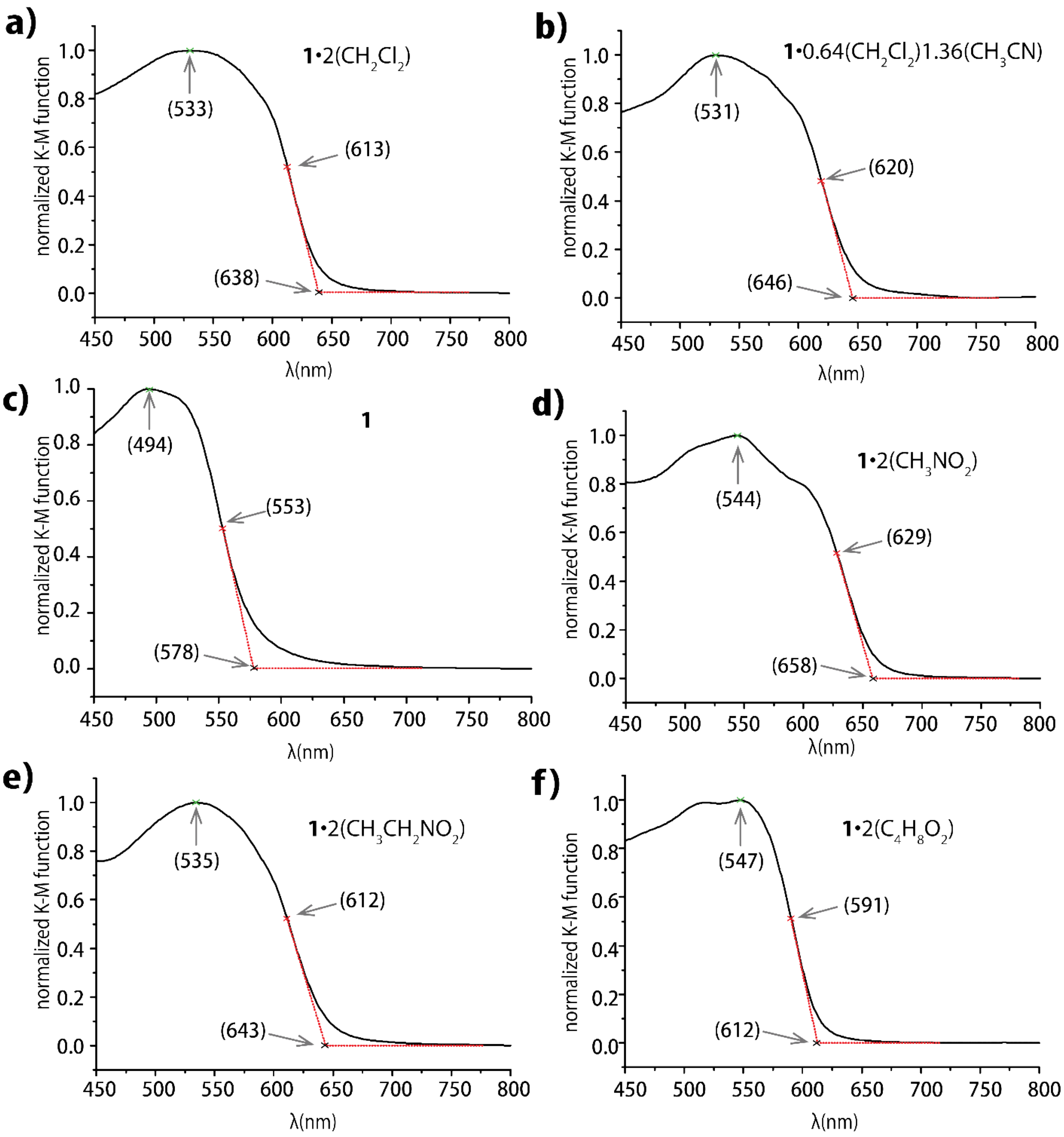

Figure S10 Solid-state diffuse reflectance UV-vis spectra of six-single crystals of **1** highlighting the λ_{max}, $\lambda_{half\text{-}height}$, and $\lambda_{on\text{-}set}$ of the CT absorption band.

Crystal structures

X-Ray Structure Determination for 1·2CH$_2$Cl$_2$.

X-ray intensity data from an intense red plate crystal were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, $\lambda = 0.71073$ Å).[3] The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[3] Final unit cell parameters were determined by least-squares refinement of 9762 reflections taken from the data set. The structure was solved by direct methods with SHELXT.[4] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014[4] using OLEX2.[5]

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space group $P2_1/n$, which was verified by structure solution. The asymmetric unit consists of half of one $C_{72}H_{54}N_2O_8$ molecule and one dichloromethane molecule of crystallization. The pyrene substituent is disordered over two closely spaced, co-planar orientations via a *ca*. 12.5° 'pivot' around *ipso* carbon C16. Populations refined to A/B = 0.760(3)/0.240(3), which were constrained to sum to unity. The geometry of the minor component was restrained to be similar to that of the major using a SHELX SAME instruction. The pairs of nearly superimposed atoms were assigned equal anisotropic displacement parameters (*eg*. U_{ij}(C17A) = U_{ij}(C17B), etc.). The dichloromethane solvent is also disordered over two positions, with a major component population of 0.861(3). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference maps before being placed in geometrically idealized positions and included as riding atoms. The largest residual electron density peak in the final difference map is 0.42 e$^-$/Å^3, located 0.71 Å from C3.

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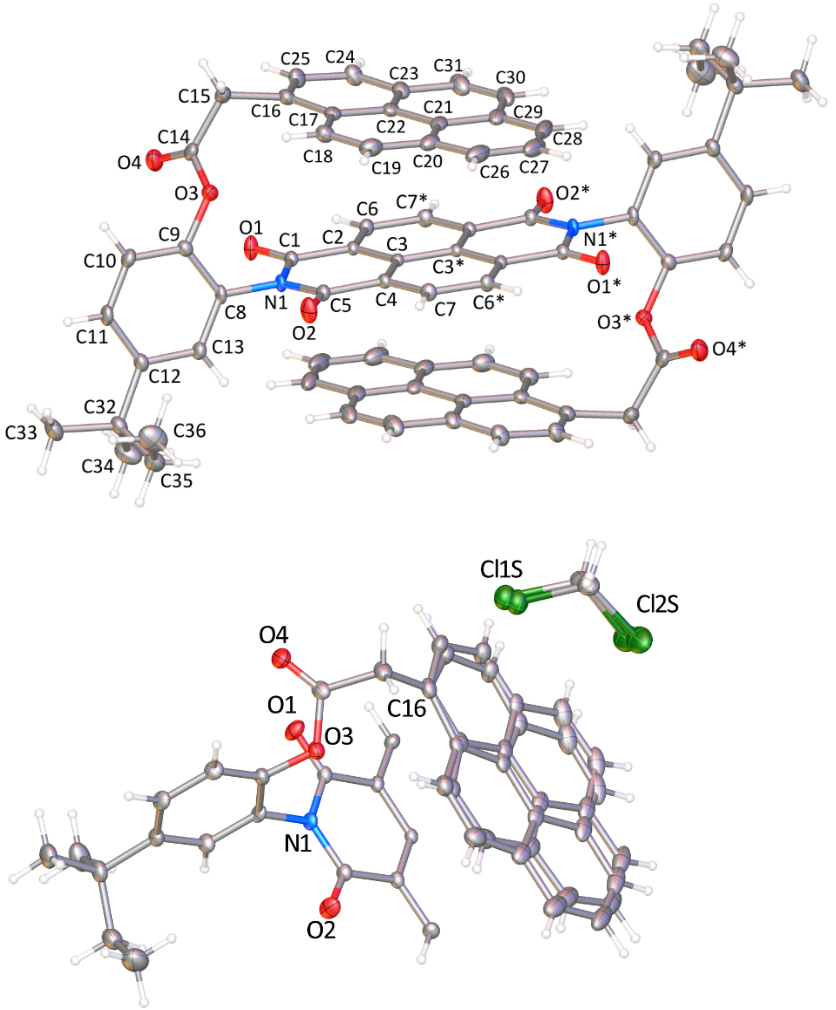
[3] APEX2 Version 2014.9-0, SAINT+ Version 8.34A and SADABS Version 2014/4. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2014

[4] Sheldrick, G. M. *Acta Crysallogr. A.* **2008**, *64*, 112.

[5] Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339


C25
C24
C23
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C30
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O4
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N1*
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C10
C3*
O1*
C8
N1
C5
C4
C7
C6*
O2
O3*
O4*
C11
C13
C12
C32
C36
C33
C34
C35
Cl1S
Cl2S
O4
C16
O1
O3
N1
O2

Table S2 Crystal data and structure refinement for **1**·$2CH_2Cl_2$.

Identification code	DFYA53_dcm_0m
Empirical formula	$C_{74}H_{58}Cl_4N_2O_8$
Formula weight	1245.02
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.1824(9)
b/Å	10.3899(5)
c/Å	17.8902(9)
α/°	90
β/°	113.491(2)
γ/°	90
Volume/Å^3	2929.1(3)
Z	2
ρ_{calc}g/cm^3	1.412
μ/mm^{-1}	0.266
F(000)	1296.0
Crystal size/mm^3	0.24 × 0.22 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.64 to 55.838
Index ranges	$-22 \leq h \leq 22$, $-13 \leq k \leq 13$, $-23 \leq l \leq 23$
Reflections collected	142111
Independent reflections	7012 [R_{int} = 0.0473, R_{sigma} = 0.0138]
Data/restraints/parameters	7012/50/457
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0931
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.0971
Largest diff. peak/hole / e Å^{-3}	0.42/-0.28

X-Ray Structure Determination for 1·2(CH_2Cl_2/CH_3CN)

X-ray intensity data from a dark red blocklike crystal were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).[6] The raw area detector data frames were reduced using the SAINT+ program.[6] Final unit cell parameters were determined by least-squares refinement of 7671 reflections from the data set. The structure was solved by direct methods with SHELXS.[4] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2013/4[4] using OLEX2.[5]

The compound crystallizes in the monoclinic space group $P2_1/n$ as determined by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of one $C_{72}H_{54}N_2O_8$ molecule, which is located on an inversion center, and a volume of disordered solvent. The -$C(CH_3)_2CH_2CH_3$ substituent of the molecule (atoms C32-C36) is disordered and was modeled with two orientations, with refined populations A/B = 0.565(9)/0.435(9). The total group population was constrained to sum to unity. Atoms near the extremity of the pyrene substituent (*eg*. near C26, C27, C28) display elongated displacement ellipsoids, suggesting some positional disorder of this substituent which becomes more pronounced farther from the attachment point (atom C16). A reasonable refinement was achieved by subjecting the anisotropic displacement parameters of pyrene atoms C19, C20, C21, C26, C27, C28, C29, C30 and C31 to an enhanced rigid-bond restraint (SHELX RIGU command), and refining one average position for the pyrene substituent. The solvent disorder was modeled with three independent groups: one acetonitrile and two dichloromethane groups. Appropriate distance restraints were applied and the total disorder site population was restrained to sum to unity. Individual occupancies refined to: N1S-C2S, 0.680(3); C3S-Cl2S, 0.242(3); C4S-Cl4S, 0.078(2). Most non-hydrogen atoms were refined with anisotropic displacement parameters, the exception being atoms of the -$C(CH_3)_2CH_2CH_3$ substituent and the disordered solvent species. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The largest residual electron density peak in the final difference map is 0.81 $e^-/Å^3$, located 0.71 Å from C1S, in the disordered solvent volume. The high reported R-factors are because of the extensive disorder within the crystal

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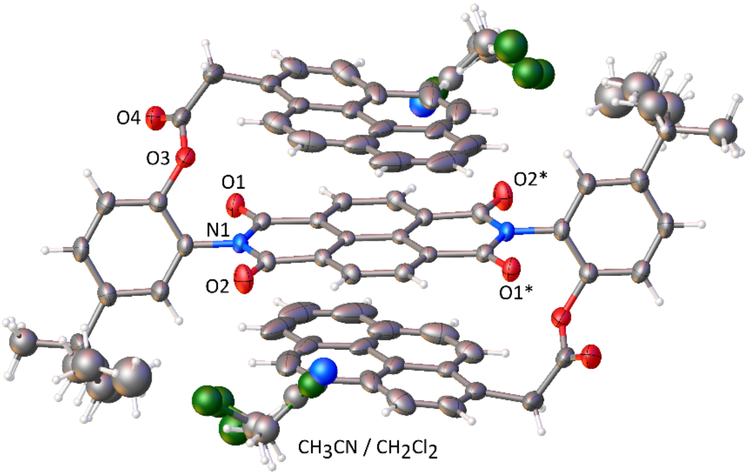
[6] SMART Version 5.630, SAINT+ Version 6.45. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.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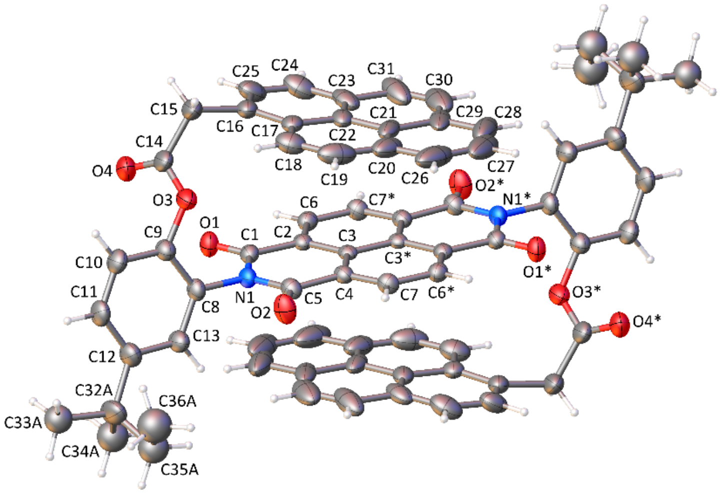
O3
O1
N1
O2
O2*
O1*
CH$_3$CN / CH$_2$Cl$_2$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C9
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C1
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C8
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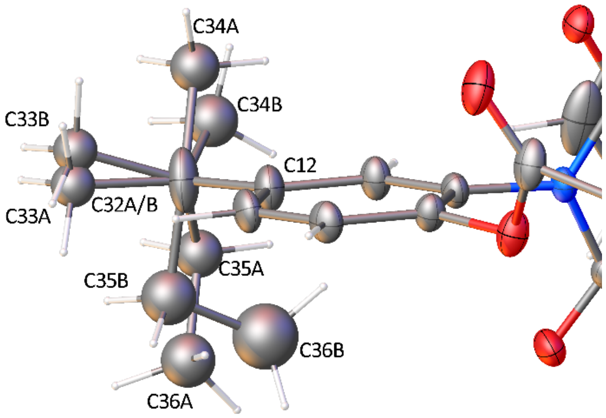
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C33B
C34B
C12
C33A
C32A/B
C35A
C35B
C36B
C36A

Table S3 Crystal data and structure refinement for **1**·2(CH_2Cl_2/CH_3CN)

Identification code	dfya53m
Empirical formula	$C_{75.36}H_{59.36}Cl_{1.28}N_{3.36}O_8$
Formula weight	1185.35
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.132(3)
b/Å	10.4771(16)
c/Å	17.718(3)
α/°	90
β/°	113.969(3)
γ/°	90
Volume/Å^3	2906.0(8)
Z	2
ρ_{calc}mg/mm^3	1.355
μ/mm^{-1}	0.144
F(000)	1242.0
Crystal size/mm^3	0.52 × 0.44 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.292 to 50.232°
Index ranges	$-20 \leq h \leq 20$, $-12 \leq k \leq 12$, $-21 \leq l \leq 21$
Reflections collected	32604
Independent reflections	5169 [R_{int} = 0.0610, R_{sigma} = 0.0354]
Data/restraints/parameters	5169/102/403
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0846, wR_2 = 0.2333
Final R indexes [all data]	R_1 = 0.1054, wR_2 = 0.2507
Largest diff. peak/hole / e Å^{-3}	0.81/-0.49

X-Ray Structure Determination for 1·

X-ray intensity data from a yellow-orange thin plate crystal of approximate dimensions 0.07 x 0.04 x 0.01 mm^3 were collected at 150K on a D8 goniostat equipped with a Bruker PHOTON100 CMOS detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to λ=0.7749Å.[7] For data collection frames in shutterless mode were measured for a duration of 5 s for data at 0.5° intervals of ω with a maximum 2θ value of ~60°. The data frames were collected using the program APEX2 and processed using the program SAINT within APEX2.[8] The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS.[8] Final unit cell parameters were determined by least-squares refinement of 7606 reflections from the data set. The structure was solved by direct methods with SHELXT.[4] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014 using OLEX2.[5]

The compound crystallizes in the triclinic system. The space group *P*-1 (No. 2) was suggested by intensity statistics and was eventually confirmed. The asymmetric unit consists of half of one molecule, which is located on a crystallographic inversion center. The molecule is disordered within the asymmetric unit. The -OC(O)CH_2(pyrene) substituent is disordered over two orientations, given atom label suffixes A and B (C14-C31, O3, O4). The disorder primarily takes the form of differently oriented but essentially co-planar pyrene groups, but also extends into the -$CH_2C(O)O$- linker. The population fraction of each orientation refined to A/B = 0.721(3)/0.279(3). The geometry of the lesser populated component was restrained to be similar to that of the major populated component using a SHELX SAME instruction. Identical pyrene substituent disorder was also observed in space group *P*1 (No. 1). The disorder is therefore not imposed by incorrect inversion symmetry and space group *P*-1 (No. 2) was retained as the proper symmetry group. The 1,1-dimethyl(propyl) substituent is also disordered, and was modeled with two components having refined populations of A/B = 0.879(4)/0.121(4). In total

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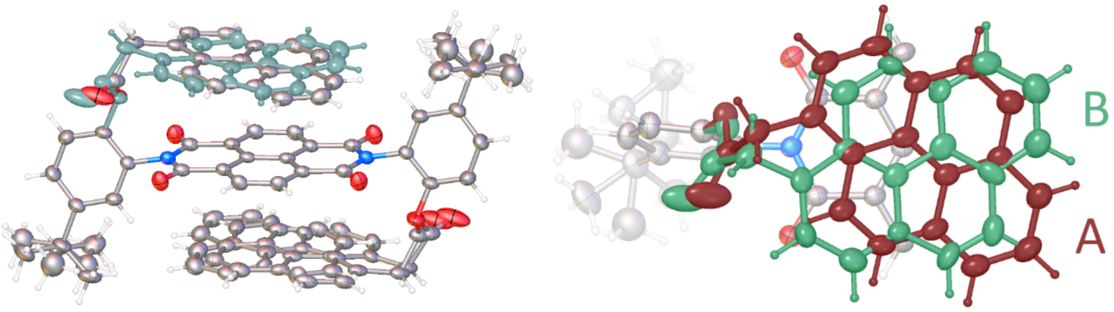
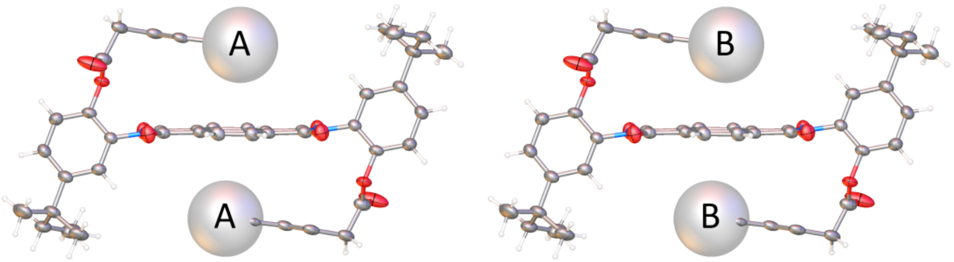
[7] Crystallographic data were collected through the SCrALS (Service Crystallography at the Advanced Light Source) program at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

[8] APEX2 v2014.7.1 and SAINT v8.34A data collection and data processing programs, respectively. Bruker Analytical X-ray Instruments, Inc., Madison, WI; SADABS v2014.4 semi-empirical absorption and beam correction program. G.M. Sheldrick, University of Göttingen, Germany.

78 geometric restraints were used to model the disorder. Non-hydrogen atoms were refined with anisotropic displacement parameters, and the ADPs of some disordered atom pairs which are nearly superimposed in the asymmetric unit were kept equal (O3A/O3B, etc.). Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The largest residual electron density peak in the final difference map is 0.26 $e^{-}/\text{Å}^{3}$, located 0.14 Å from O4B.



All molecules are genuinely centrosymmetric and 72% of all molecules throughout the crystal have the pyrene group “A” conformation on both sides on the central plane. These are disordered on the same site throughout the crystal with 28% of molecules having both pyrene groups in conformation B on both sides of the central plane:



72%

28%

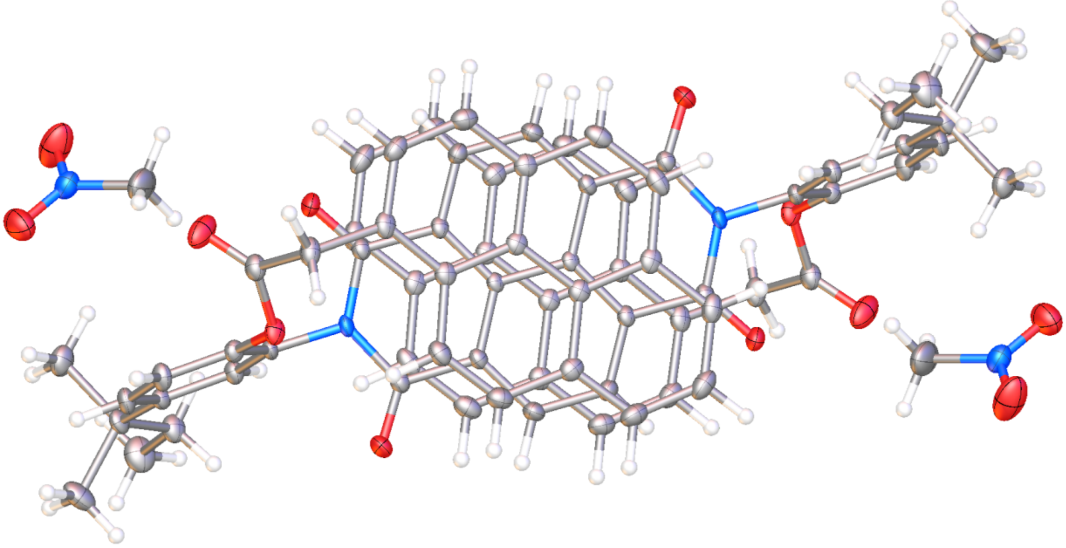
Table S4 Crystal data and structure refinement for **1**.

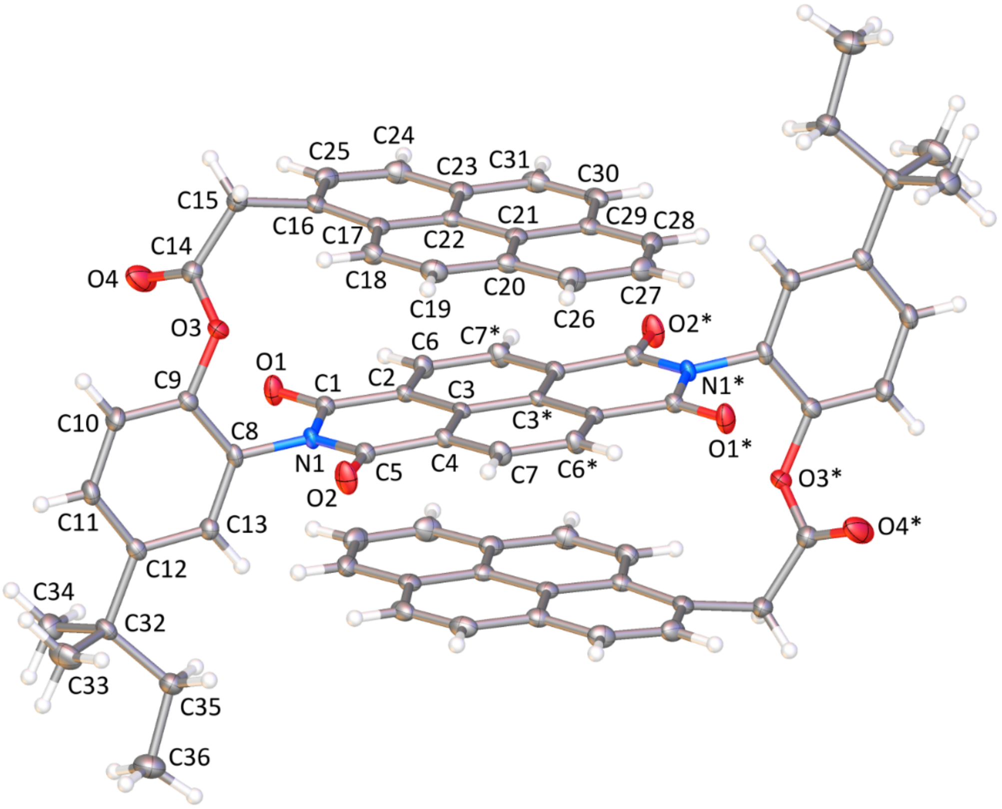
Identification code	usca048_0m
Empirical formula	$C_{72}H_{54}N_2O_8$
Formula weight	1075.17
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.4849(7)
b/Å	12.6610(11)
c/Å	13.7331(12)
α/°	108.388(2)
β/°	98.716(2)
γ/°	104.328(2)
Volume/Å^3	1313.5(2)
Z	1
ρ_{calc}g/cm^3	1.359
μ/mm^{-1}	0.107
F(000)	564.0
Crystal size/mm^3	0.07 × 0.04 × 0.01
Radiation	synchrotron ($\lambda = 0.7749$)
2Θ range for data collection/°	4.178 to 58.446
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$
Reflections collected	21985
Independent reflections	5423 [$R_{int} = 0.0396$, $R_{sigma} = 0.0433$]
Data/restraints/parameters	5423/78/537
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	$R_1 = 0.0518$, $wR_2 = 0.1141$
Final R indexes [all data]	$R_1 = 0.0824$, $wR_2 = 0.1266$
Largest diff. peak/hole / e Å^{-3}	0.26/-0.29

X-Ray Structure Determination for 1·2(CH_3NO_2)

X-ray intensity data from a red plate crystal were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo Ka radiation, l = 0.71073 Å).[3] The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[3] Final unit cell parameters were determined by least-squares refinement of 9907 reflections taken from the data set. The structure was solved by direct methods with SHELXT.[4] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014[4] using OLEX2.[5]

The compound crystallizes in the triclinic system. The space group *P*-1 was determined by structure solution. The asymmetric unit consists of half of one $C_{72}H_{54}N_2O_8$ molecule, which is located on a crystallographic inversion center, and one nitromethane molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference maps before being included as riding atoms. The largest residual electron density peak in the final difference map is 0.42 $e^-/Å^3$, located 0.72 Å from C31.




C25
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C7*
O1
C1
C2
N1*
C9
C3
C10
C8
C3*
O1*
N1
C5
C4
C7
C6*
O3*
O2
C11
C13
O4*
C12
C34
C32
C33
C35
C36

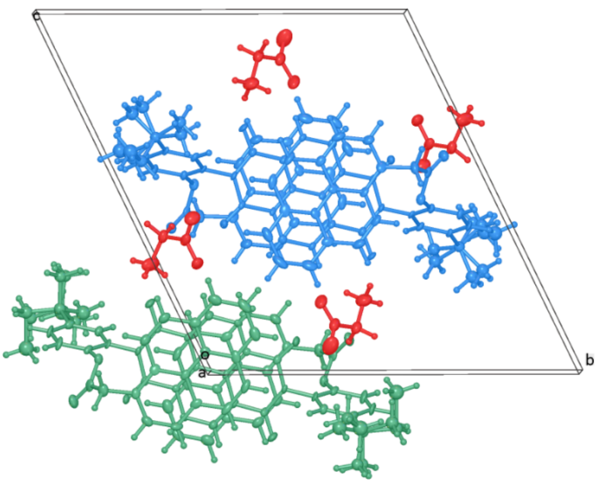
Table S5 Crystal data and structure refinement for **1**·2(CH_3NO_2)

Identification code	DFYA53_MeNO2_0m
Empirical formula	$C_{74}H_{60}N_4O_{12}$
Formula weight	1197.26
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.0093(4)
b/Å	10.5133(4)
c/Å	16.3672(7)
α/°	71.388(2)
β/°	89.742(2)
γ/°	62.504(2)
Volume/Å^3	1426.83(10)
Z	1
ρ_{calc}g/cm^3	1.393
μ/mm^{-1}	0.095
F(000)	628.0
Crystal size/mm^3	0.62 × 0.44 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.48 to 55.102
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	27328
Independent reflections	6558 [R_{int} = 0.0352, R_{sigma} = 0.0256]
Data/restraints/parameters	6558/0/411
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.1136
Final R indexes [all data]	R_1 = 0.0484, wR_2 = 0.1187
Largest diff. peak/hole / e Å^{-3}	0.42/-0.33

X-Ray Structure Determination for 1·2(EtNO$_2$)

X-ray intensity datasets from dark red tablet crystals were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å).[3] Several crystals from three separate crystallization processes were examined; three datasets were collected and the best reported here. Each crystal showed broad diffraction peaks, often with multiple maxima, consistent with lamellar twinning of the platelike specimens. Efforts to cleave a single domain apart were not successful. The best crystal was found to consist primarily of two non-merohedrical twin domains. The unit cells and orientation matrices for each domain and the twin law relating reflections of the two were derived with the Bruker Cell_Now program.[3] The twin law is (1 0 0 / -0.117 -1 0 / -0.033 0 -1). The major twin fraction refined to 0.522(2). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the SAINT+ and TWINABS programs.[3] Negligible diffraction intensity was observed above $2\theta_{\max}$ = 48.5° and the dataset was truncated at that value. Final unit cell parameters were determined by least-squares refinement of 9437 reflections taken from both domains. The structure was solved by direct methods with SHELXS.[4] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014[4] using OLEX2.[5]

The compound crystallizes in the triclinic system. The space group *P*-1 was confirmed by structure solution. The asymmetric unit consists of half each of two crystallographically independent $C_{72}H_{54}N_2O_8$ molecules, each on an inversion center, and two independent nitroethane molecules. The $C_{72}H_{54}N_2O_8$ molecules were numbered similarly except for label suffixes A or B. The $-C(CH_3)_2(CH_2CH_3)$ substituents of each independent molecule are rotationally disordered and were modeled with two components each. 63 distance and isotropic displacement parameter restraints were used to maintain chemically reasonable group geometries for these species. A further 60 'rigid-bond' restraints (Shelx RIGU) were applied to 10 atoms of molecule “B” to prevent physically senseless anisotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters except for disordered atoms (isotropic). Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The largest residual electron density peak in the final difference map is 0.46 $e^-/Å^3$, located 0.37 Å from H34D. The high final *R*-values arise because of low crystallinity related to the twinning and disorder observed in the material.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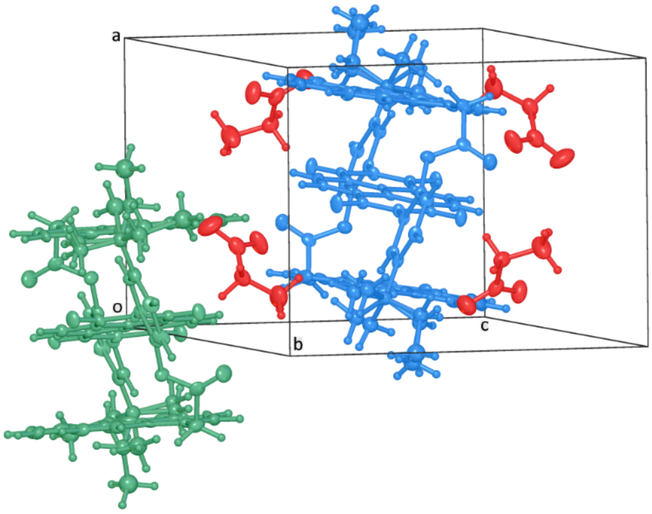
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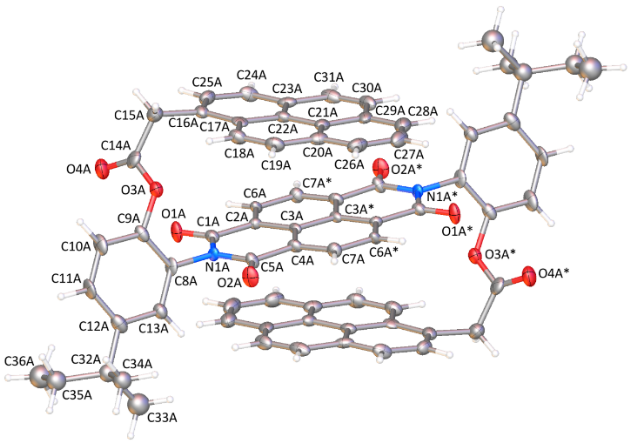
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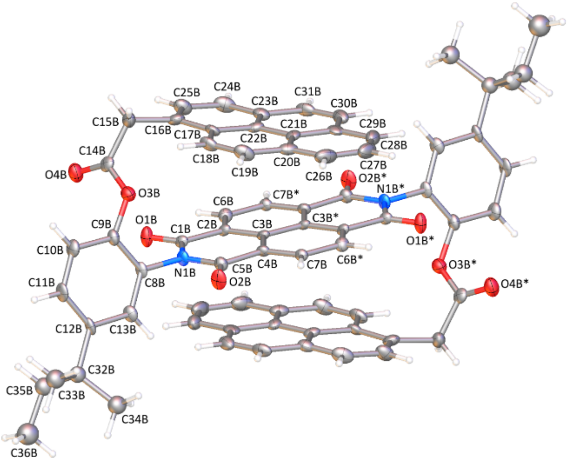
C33A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C5B
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O4B*
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C12B
C13B
C32B
C35B
C33B
C34B
C36B

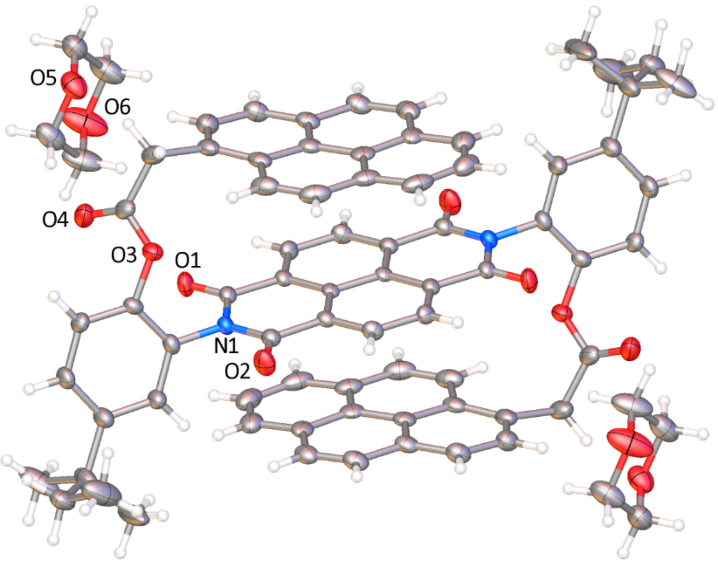
Table S6 Crystal data and structure refinement for **1**·2($EtNO_2$).

Identification code	twin5a
Empirical formula	$C_{76}H_{64}N_4O_{12}$
Formula weight	1225.31
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.3369(14)
b/Å	17.1080(18)
c/Å	18.463(2)
α/°	115.858(3)
β/°	90.538(4)
γ/°	92.053(4)
Volume/Å^3	2935.1(6)
Z	2
ρ_{calc}g/cm^3	1.386
μ/mm^{-1}	0.094
F(000)	1288.0
Crystal size/mm^3	0.44 × 0.18 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.442 to 48.814
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 17$, $0 \leq l \leq 21$
Reflections collected	9684
Independent reflections	9684 [R_{int} = 0.0546, R_{sigma} = 0.0739]
Data/restraints/parameters	9684/129/811
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0765, wR_2 = 0.1916
Final R indexes [all data]	R_1 = 0.0974, wR_2 = 0.2059
Largest diff. peak/hole / e Å^{-3}	0.46/-0.38

X-Ray Structure Determination for 1·2($C_2H_4O_2$)

X-ray intensity data from a thin red plate crystal were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å).[3] The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[3] Final unit cell parameters were determined by least-squares refinement of 9970 reflections taken from the data set. The structure was solved by direct methods with SHELXS.[4] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014[4] using OLEX2.[5]

The compound crystallizes in the monoclinic space group $P2_1/c$ as determined by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of one $C_{72}H_{54}N_2O_8$ molecule located on a crystallographic inversion center, and one dioxane molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference maps before being included as riding atoms. The largest residual electron density peak in the final difference map is 0.43 $e^-/Å^3$, located 0.58 Å from H34C.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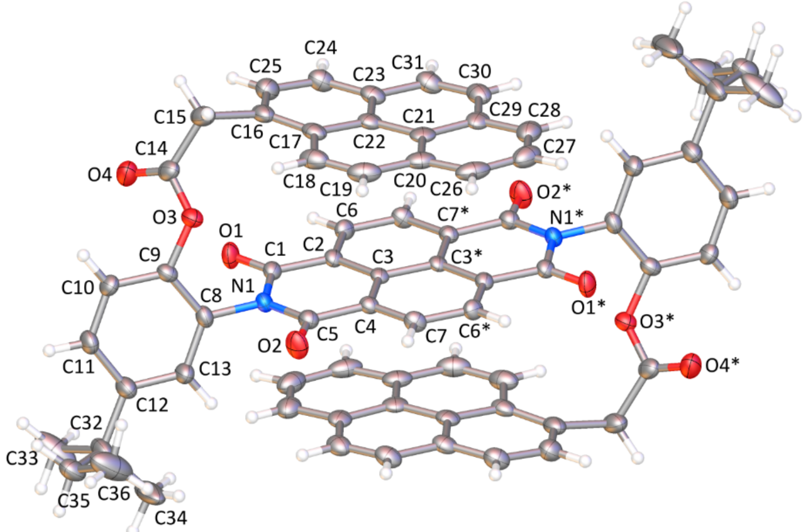
N1
O2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C8
O1*
O3*
C5
C4
C7
C6*
O2
O4*
C11
C13
C12
C32
C33
C35
C36
C34

Table S7 Crystal data and structure refinement for **1**·2($C_2H_4O_2$).

Identification code	DFYA53c
Empirical formula	$C_{80}H_{70}N_2O_{12}$
Formula weight	1251.38
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.978(2)
b/Å	16.7517(19)
c/Å	10.8751(13)
α/°	90
β/°	92.952(4)
γ/°	90
Volume/Å^3	3088.8(6)
Z	2
ρ_{calc}g/cm^3	1.345
μ/mm^{-1}	0.090
F(000)	1320.0
Crystal size/mm^3	0.44 × 0.4 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.47 to 50.134
Index ranges	$-20 \leq h \leq 20$, $-19 \leq k \leq 19$, $-12 \leq l \leq 12$
Reflections collected	47356
Independent reflections	5462 [R_{int} = 0.0552, R_{sigma} = 0.0270]
Data/restraints/parameters	5462/0/427
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1= 0.0487, wR_2 = 0.1156
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1239
Largest diff. peak/hole / e Å^{-3}	0.43/-0.33

X-Ray Structure Determination for 2

X-ray intensity data from a colourless tablet were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[6] The raw area detector data frames were reduced with the SAINT+ and SADABS programs.[6] Final unit cell parameters were determined by least-squares refinement of 7254 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXS/L[4] within OLEX2.[5]

The compound crystallizes in the monoclinic space group $P2_1/c$ as determined by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of one molecule, which is located on a crystallographic inversion center. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference maps before being placed in geometrically idealized positions and included as riding atoms. The largest residual electron density peak of 0.36 e$^-$/Å^3 in the final difference map is located 0.71 Å from C3.

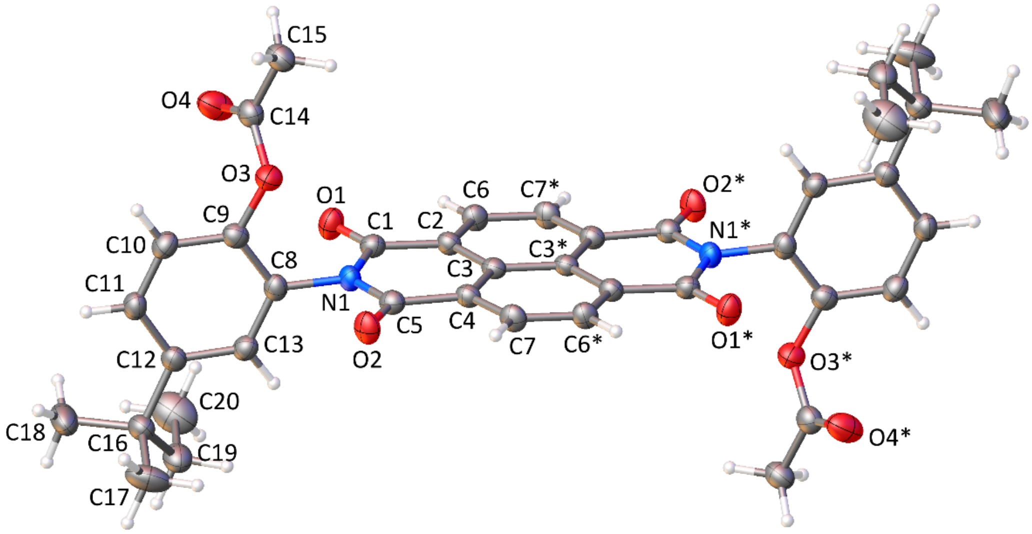

Table S8 Crystal data and structure refinement for **2**

Identification code	BTMA25s
Empirical formula	$C_{40}H_{38}N_2O_8$
Formula weight	674.72
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.0743(16)
b/Å	15.186(3)
c/Å	12.460(2)
α/°	90.00
β/°	106.575(3)
γ/°	90.00
Volume/Å^3	1645.8(5)
Z	2
ρ_{calc}mg/mm^3	1.362
μ/mm^{-1}	0.095
F(000)	712.0
Crystal size/mm^3	0.54 × 0.4 × 0.24
2Θ range for data collection	4.34 to 52.92°
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 19$, $-15 \leq l \leq 15$
Reflections collected	23130
Independent reflections	3402[R(int) = 0.0337]
Data/restraints/parameters	3402/0/230
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	$R_1 = 0.0458$, $wR_2 = 0.1205$
Final R indexes [all data]	$R_1 = 0.0526$, $wR_2 = 0.1263$
Largest diff. peak/hole / e Å^{-3}	0.36/-0.19

1H and 13C NMR Spectra.

1H and 13C NMR spectra of 1

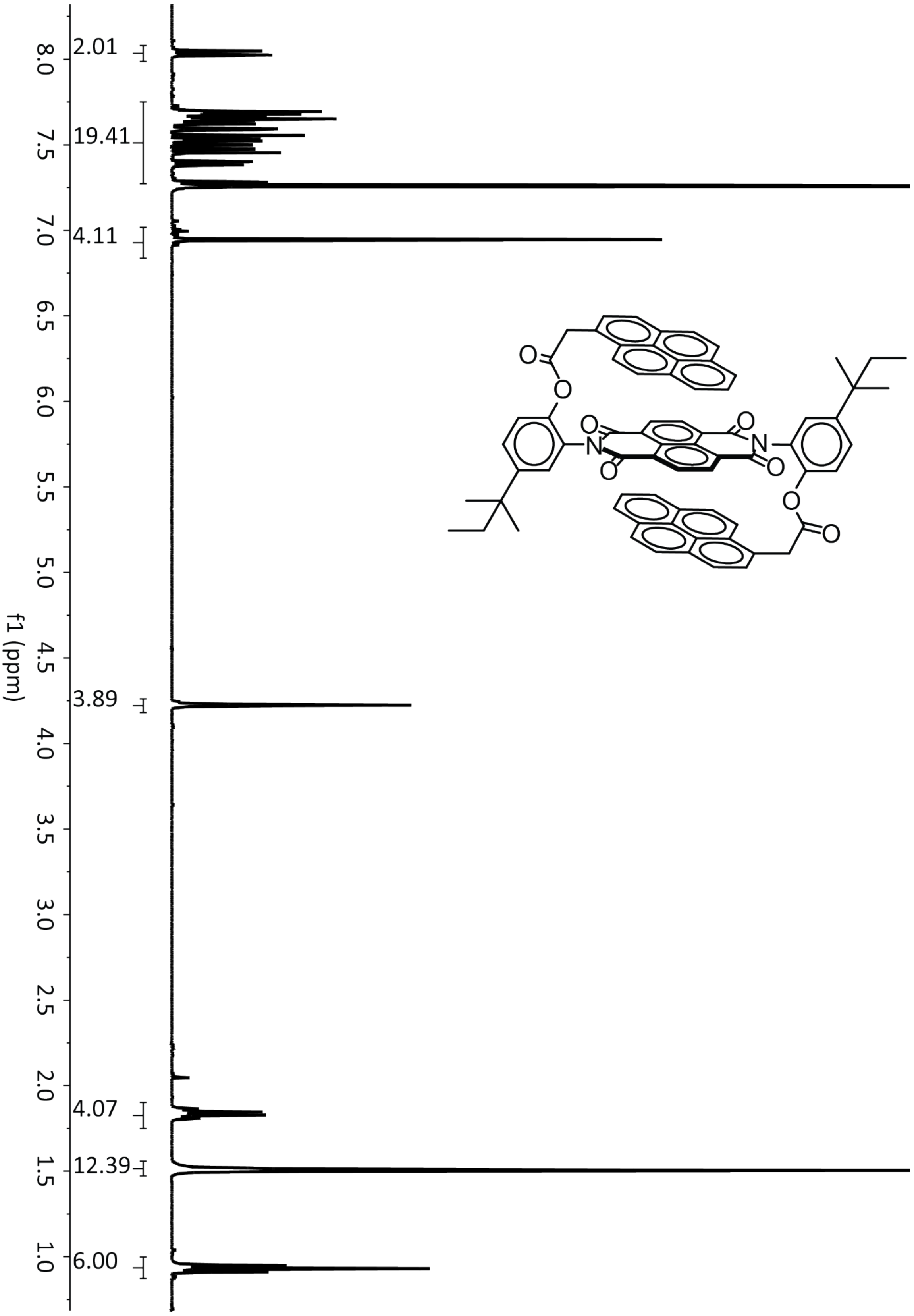

Figure S 11 ^{1}H NMR spectrum of **1** ($CDCl_3$, 400 MHz)

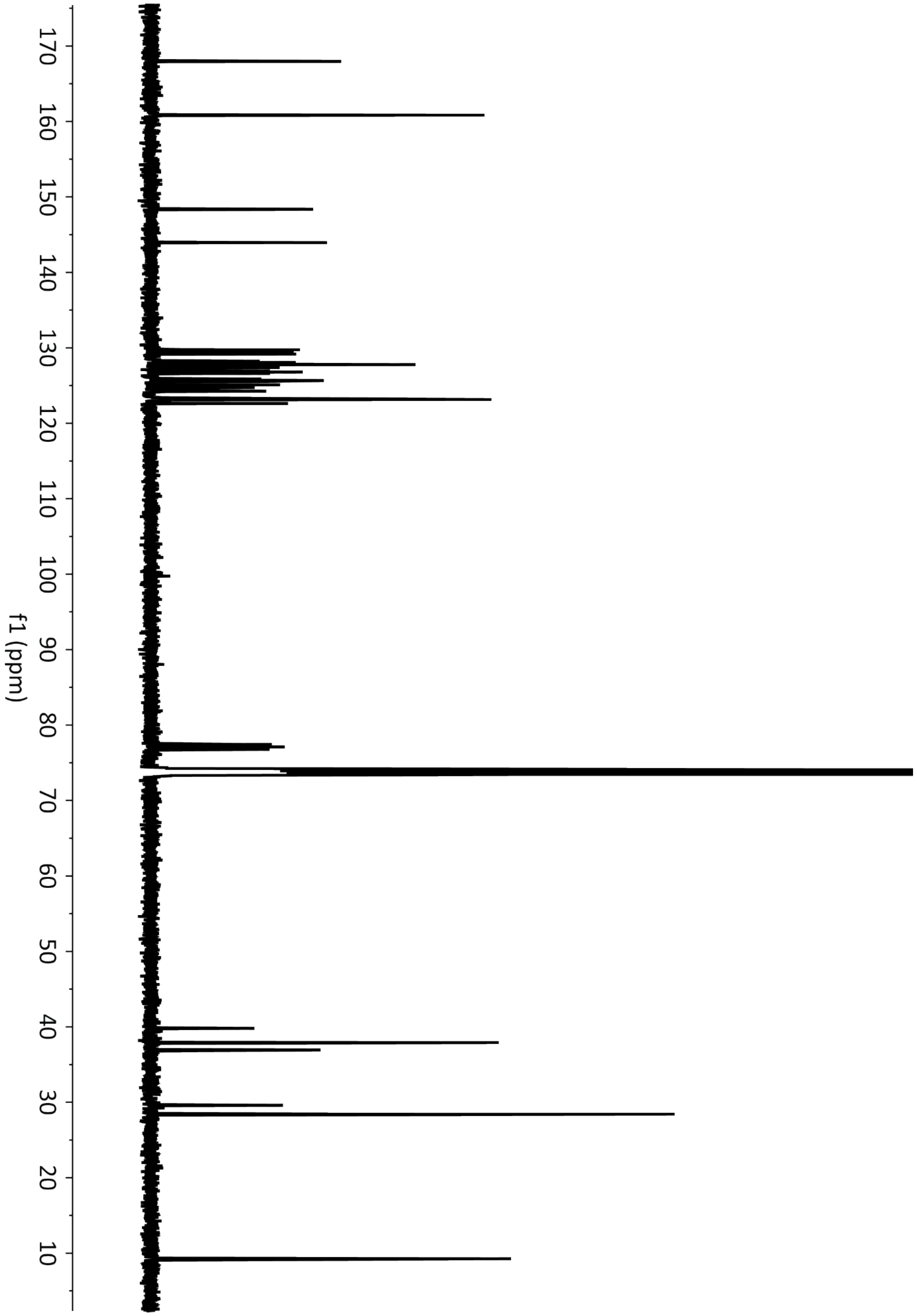

Figure S 12 ^{13}C NMR spectrum of **1**(TCE-d_2, 100 MHz)

1H and 13C NMR spectra of 2

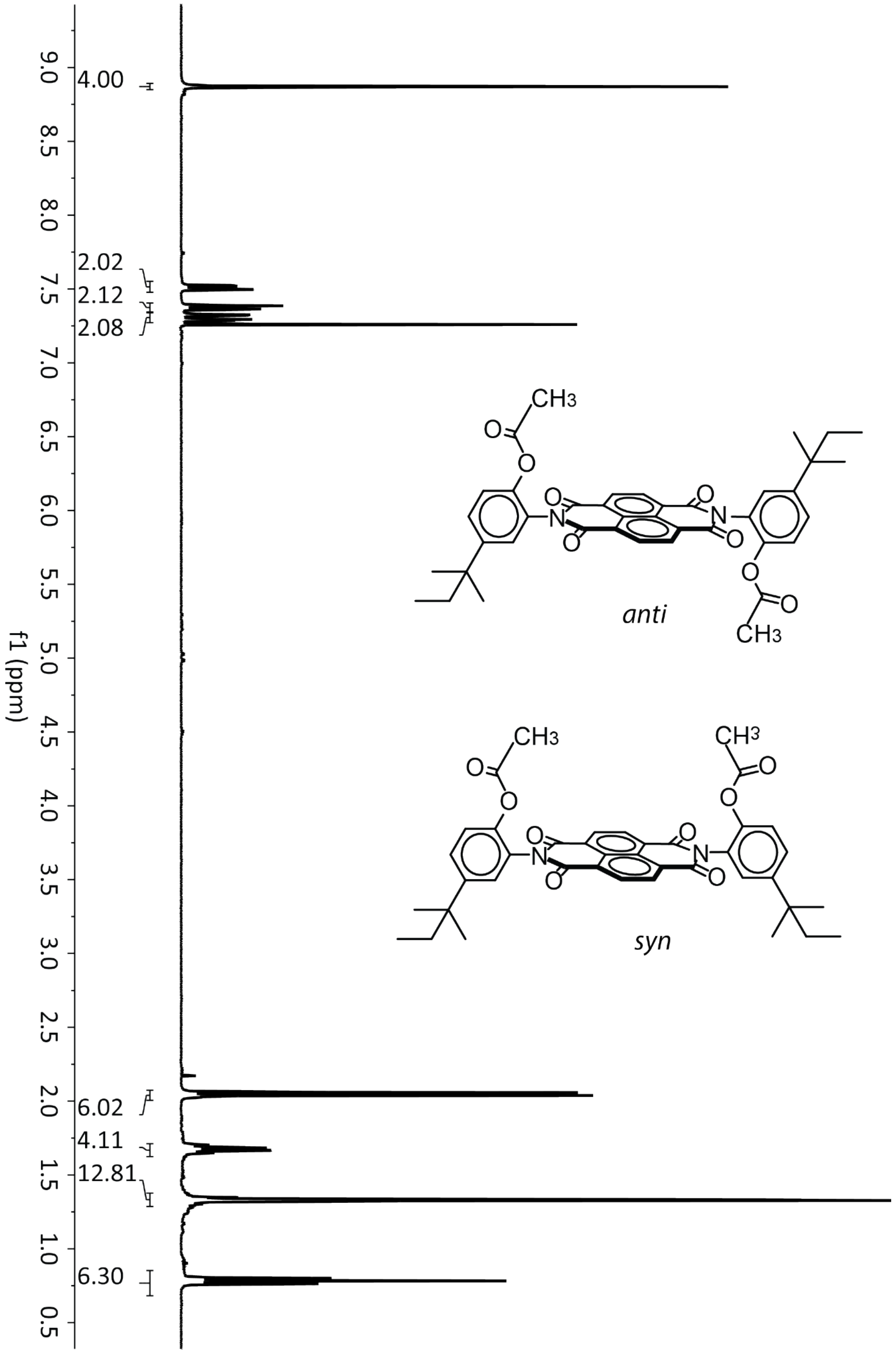

Figure S 13. ^{1}H NMR spectrum of **2** ($CDCl_3$, 400 MHz)

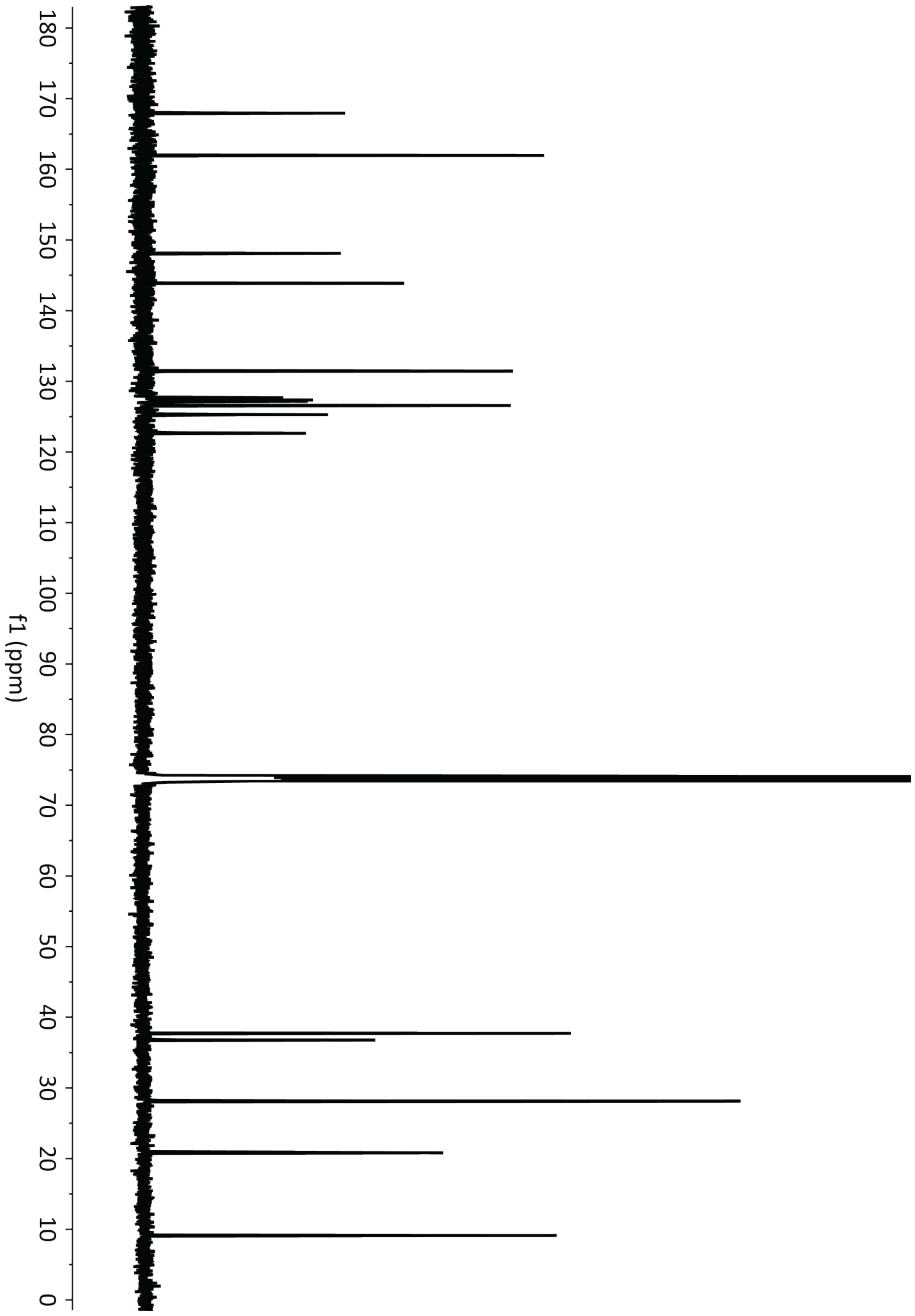

Figure S 14. ^{13}C NMR spectrum of **2** (TCE-d_2, 100 MHz)