Supplementary Information

One-step, green synthesis of a supramolecular organogelator based on mellitic triimide for the recognition of aromatic compounds

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Table S1 Instruments

Instruments	Brands and Types	Conditions
Purification		Three-zone sublimation apparatus
Elemental Analyses	Perkin Elmer 2400 series II CHNS/O elemental analyzer	
MS	JEOL JMS-T100GC	Direct probe ionization, FD-MS
^{1}H NMR ^{13}C NMR	JEOL 500 MHz JNM-ECX	Chemical shifts were calibrated to the corresponding deuterated solvents
TGA DSC	TA instruments SDT Q600 unit	Under a N_2 atmosphere with a heating rate of 10 °C per minute
FE-SEM	JEOL 7600-FE	15.0 kV
XRD	Rigaku Smart Lab Diffractometer	45 kV and 200 mA using CuKα radiation

Table S2 Materials

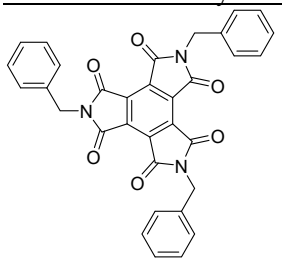
Reagents	**CAS No.**	**Supplier, code and Grade**
Mellitic acid	517-60-2	Tokyo Kasei Co., Ltd., B0246, >98.0%
Benzylamine	100-46-9	Tokyo Kasei Co., Ltd., B0406, >99.0%
4-Fluorobenzylamine	140-75-0	Tokyo Kasei Co., Ltd., F0252, >98.0%

All chemicals were obtained from commercial sources and were used as received.

Methods S1 Synthesis

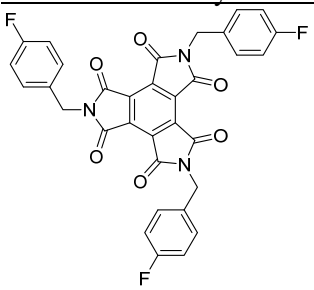
Mellitic triimide derivatives were synthesized according to the literature.[1]

Procedure for the synthesis of tribenzyl-mellitic-triimide (**1**)



To mellitic acid (4.99 g, 14.6 mmol) in water (100 ml) was added benzylamine (4.76 g, 44.4 mmol) and the reaction mixture was stirred for 10 min at room temperature. After removing solvent in vacuo, the colorless solid was heated at 140 °C for 96 h. The crude product was purified by sublimation. Further purification was optionally accomplished by column chromatography with dry loading on a silica gel using hexane/ethyl acetate mixture (1:2) and recrystallization from dichloromethane/hexane to give pure product as yellow crystals (1.62 g, 20.0%).
Mp: 293–296 °C. MS/FD: m/z 555 (M^+, 100%). ^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$, Me_4Si) = 7.48 (d, J = 7.9 Hz, 6H), 7.32–7.26 (m, 9H), 4.91 (s, 6H). ^{13}C-NMR: δ/ppm (125 MHz, $CDCl_3$) = 162.2, 135.0, 133.6, 129.5, 128.9, 128.6, 43.1. Anal. Calcd. For $C_{33}H_{21}N_3O_6$: C, 71.35; H, 3.81; N, 7.56; O, 17.28. Found: C, 71.05; H, 3.65; N, 7.50.

Procedure for the synthesis of tris(4-fluorobenzyl)-mellitic-triimide (**2**)



Mellitic triimide **2** was synthesized in 32.2% yield as yellow crystals by the similar method for **1**.
Mp: 313–318 °C. MS/FD: m/z 609 (M^+, 100%). ^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$, Me_4Si) = 7.47 (dd, J = 5.3 Hz, J = 8.7 Hz, 6H), 6.97 (dd, J = 8.7 Hz, 6H), 4.90 (s, 6H). ^{13}C-NMR: δ/ppm (125 MHz, $CDCl_3$) = 163.8, 162.1, 161.8, 133.6, 131.6, 131.5, 130.8, 130.8, 116.0, 115.9, 42.3. Anal. Calcd. For $C_{33}H_{18}F_3N_3O_6$: C, 65.03; H, 2.98; F, 9.35; N, 6.89; O, 15.75. Found: C, 64.77; H, 2.62; N, 6.87.

[1] K. G. Rose, D. A. Jaber, C. A. Gondo and D. G. Hamilton, *J. Org. Chem.,* 2008, **73**, 3950.

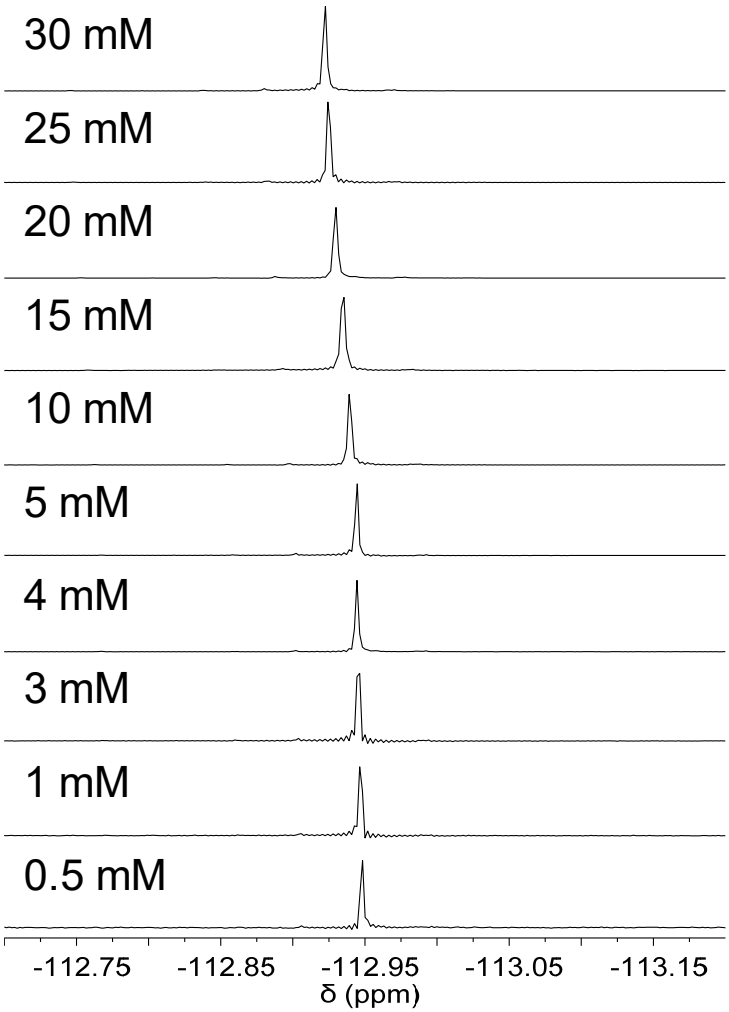
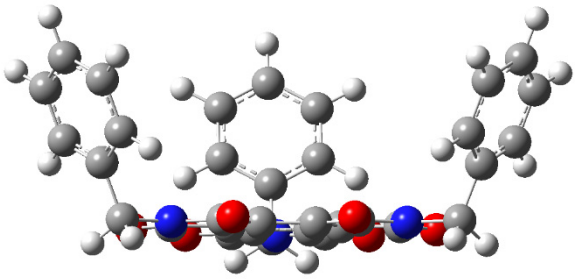
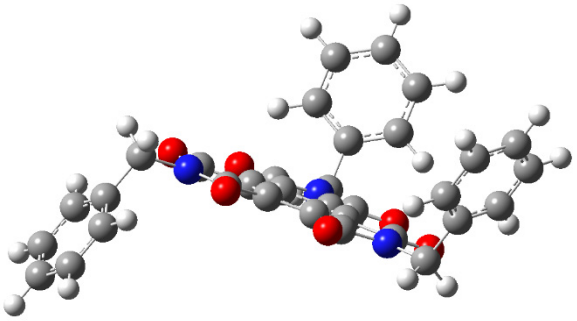
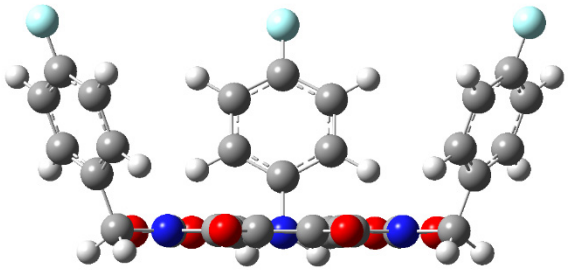
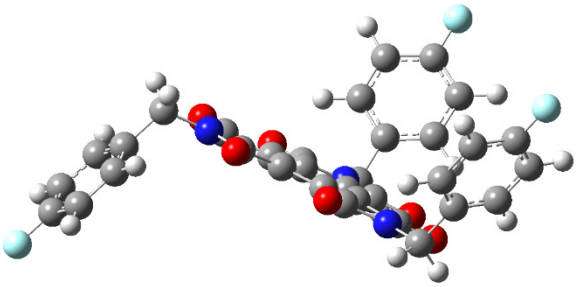


Fig. S1 ^{19}F NMR (470 MHz, trichlorofluoromethane as standard) spectra of **2** at various concentrations in chloroform-*d* at r.t.

Methods S2 Computational Chemistry

Molecular orbital Calculations were performed using the program Gaussian 09.[1] The geometry optimization and single point energy were calculated at the B3LYP/6-31+G(d,p) level.[2] The presence of energy minima was confirmed by the absence of imaginary modes (no imaginary frequencies).

Table S3 Optimized geometry and single point energy for bowl and chair conformations of compound **1** and **2**

Bowl conformation	Chair conformation
	
-1885.94394105 hartree	-1885.94400287 hartree
	
-2183.66494772 hartree	-2183.66498878 hartre

[2] Gaussian 09, Revision C.01: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Table S4 Gelation properties of compound **2** in various organic solvents

Solvent	Phase[a]	Phase[b]	Solvent	Phase[a]	Phase[b]
Chloroform	S	G	Acetonitrile	S	IM
DCM	S	S	DMSO	S	IM
Benzene	S	S	Methanol	I	–
Toluene	S	S	Ethanol	I	–
THF	S	S	Hexane	I	–
Acetone	S	S	Diethyl ether	I	–
Ethyl acetate	S	S			

[a] Single solvent. [b] upon addition of hexane. S, solution; G, gel; I, insoluble; IM, immiscible.

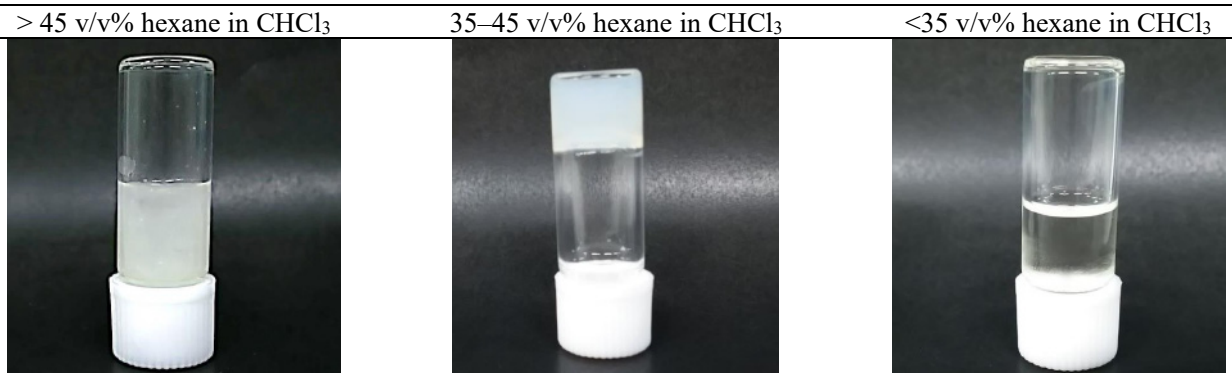


Fig. S2 Photograph of compound **2** in chloroform-hexane mixed solvent with different solvent ratio conditions.

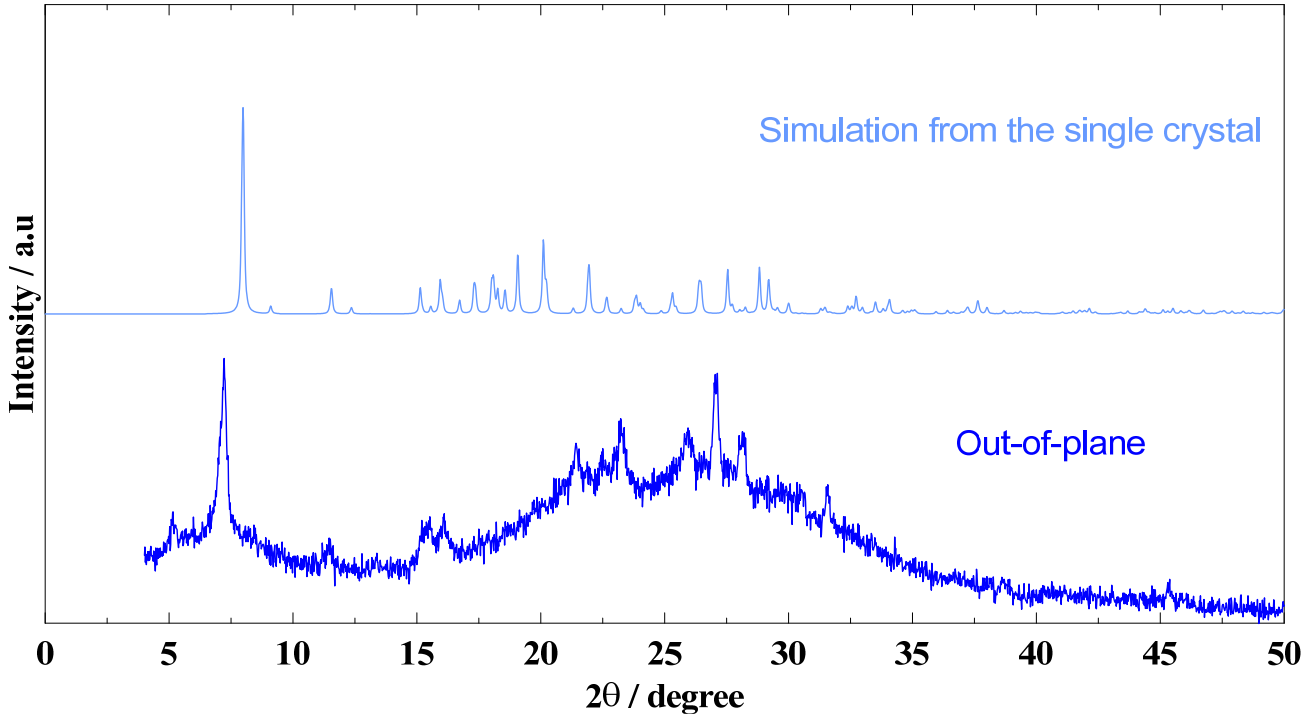


Fig. S3 X-ray diffraction of xerogel and simulated pattern from the single crystal XRD data for compound **2**.

Methods S3 X-ray Crystallographic Structure Determination

Suitable crystals were selected under Paratone® N (Hampton Research catalog number HR2-643), under ambient conditions and attached to the tip of a MiTeGen MicroMount©. X-ray diffraction data for OXCMA were collected on a Rigaku Saturn 724 CCD diffractometer with Mo-Kα radiation (λ = 0.71075 Å). Data collection, cell refinement, and data reduction were carried out using the CrystalClear-SM software. The structure was solved by direct methods using the program SHELXS-97, and refined by full-matrix least squares methods on F2 using SHELXL-97. All materials for publication were prepared by Yadokari-XG 2009 software. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated geometrically and refined as a riding model. X-ray crystallographic information files (CIFs) are available. CCDC nos. 1557859–1557873 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

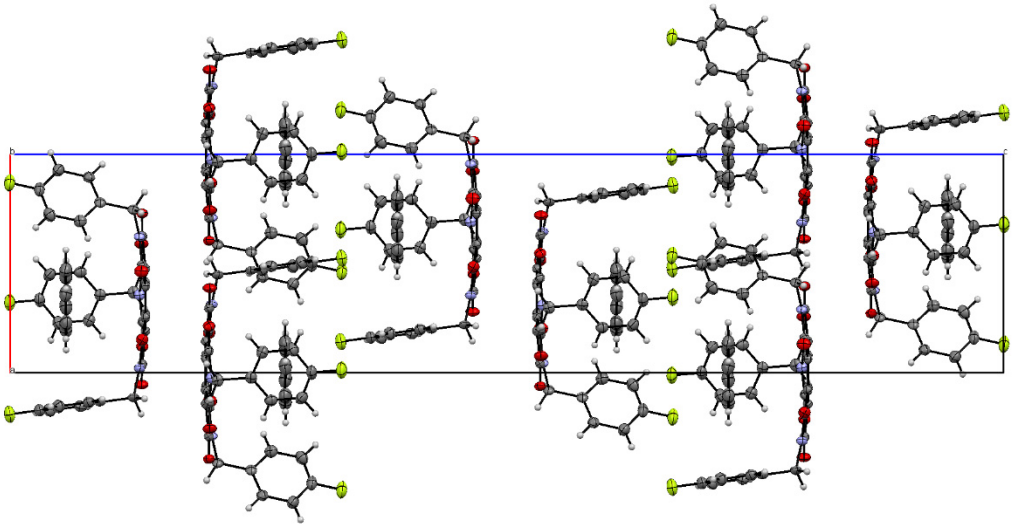


Fig. S4 Typical packing motif of mellitic triimide•aromatic molecule complex with *R*-3 space group.

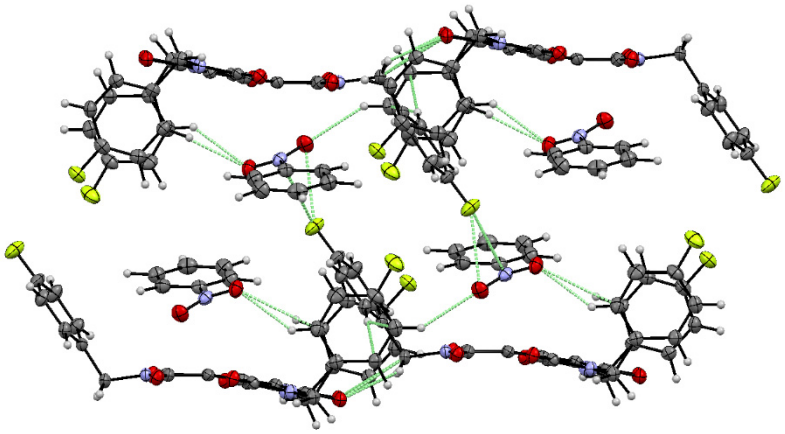


Fig. S5 The packing structure of **2**•nitrobenzene. The green dashed lines show the short contacts such as C—H···O, C—F···O, and C—F···N.

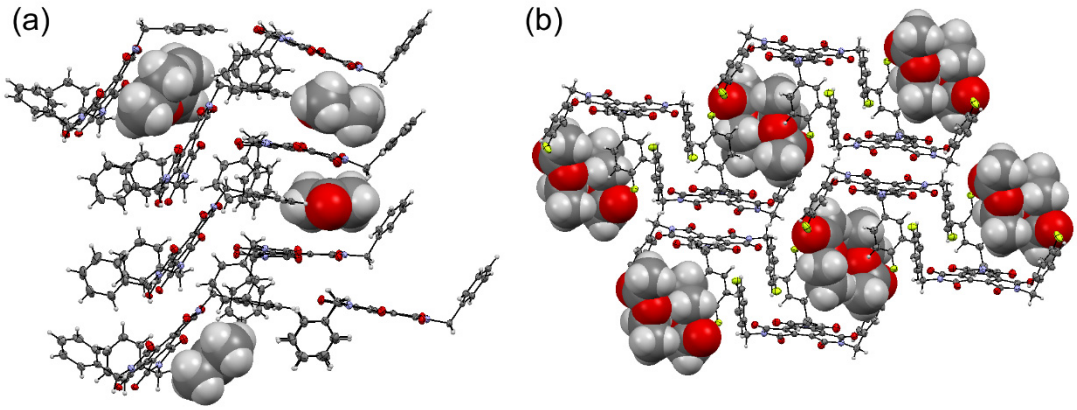


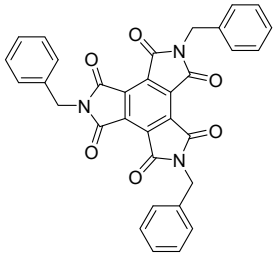
Fig. S6 The packing structure of **1**•acetone and **2**•EtOAc.

Table S5 Crystal descriptions and distance measured in the mellitic triimides **1**•aromatic guest and **2**•aromatic guest

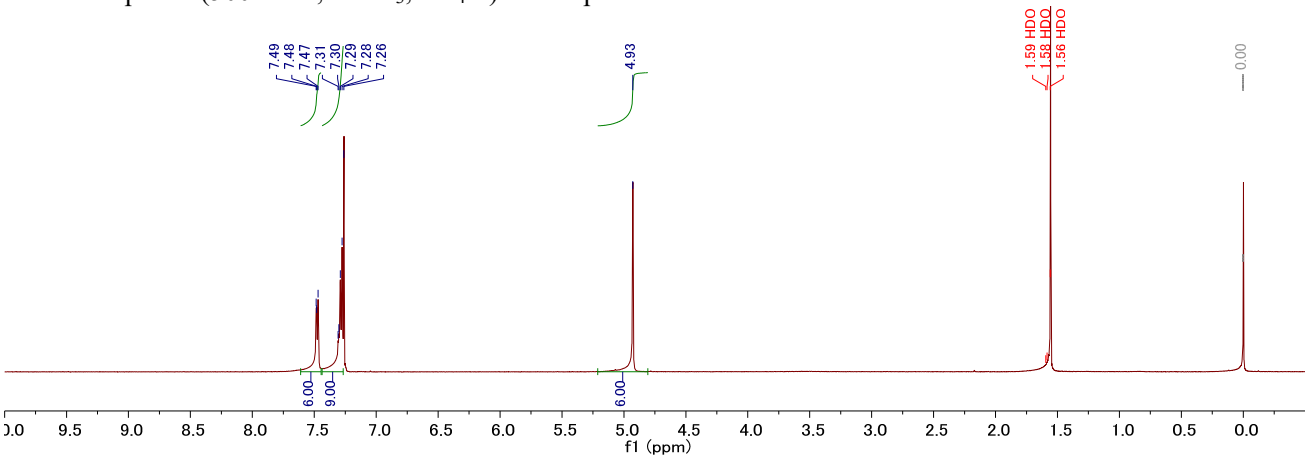
Crystals	Crystal Description	Crystal Growth	Space Group	d_1 (π-π) [Å][a]	d_2 (CH–π) [Å][a]	θ [°][a]	ϕ [°][a]
1-form I	platelet/ yellow	sublimation	$P2_12_12_1$	–	–	110.9–116.4	56.2–88.6
1-form II	block/orange	sublimation	$P2_1/c$	–	–	112.5–121.8	41.6–88.8
2	needle/ colorless	sublimation	$P2_1$	–	–	110.3–121.4	47.8–80.6
1•C_6H_6	prism/ colorless	slow evaporation	*R*-3	3.42	3.01	106.8	69.2
1•$C_6H_5CH_3$	prism/ colorless	solvent diffusion	*R*-3	3.44	2.87, 2.96, 3.68	107.1	73.5
1•C_6H_5Cl	prism/ colorless	slow evaporation	*R*-3	3.39	2.57, 2.84, 3.58	106.2	71.9
1•$C_6H_5NH_2$	prism/orange	slow evaporation	*R*-3	3.35	2.86, 3.16	106.7	71.0
1•C_5H_5N	prism/ colorless	slow evaporation	*R*-3	3.37	2.87, 3.00, 3.21	106.9	69.9
1•Acetone	block/orange	slow evaporation	$P2_12_12_1$	–	–	107.0–120.3	67.9–89.4
2•C_6H_6	prism/ colorless	slow evaporation	*R*-3	3.42	3.02	107.3	69.2
2•$C_6H_5CH_3$	prism/ colorless	slow evaporation	*P*-1	3.25–3.48	2.87, 2.90	105.1–111.3	65.9–80.6
2•C_6H_5Cl	prism/ yellow	solvent diffusion	*R*-3	3.48	2.68, 2.99, 3.66	107.2	72.1
2•C_5H_5N	prism/ yellow	slow evaporation	*R*-3	3.40	2.91, 3.06, 3.24	107.8	67.4
2•$C_6H_5NO_2$	prism/ colorless	slow evaporation	$P2_1/n$	3.09–3.86	2.86	108.5–122.8	48.5–77.4
2•EtOAc	platelet/ colorless	slow evaporation	$P2_1/n$	–	–	111.3–124.2	60.4–80.3

[a] Positions indicated in the Fig. 5. θ indicates the angle among phenyl ring centroids

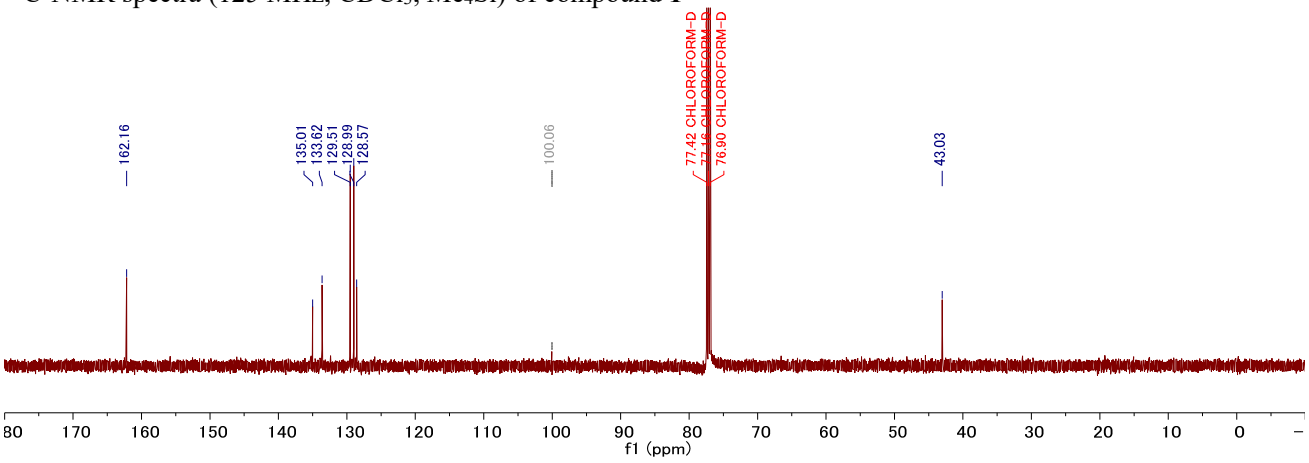
Data S1　NMR Spectra

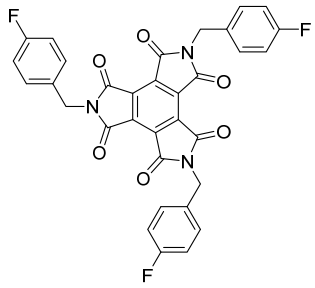


^{1}H-NMR spectra (500 MHz, $CDCl_3$, Me_4Si) of compound **1**

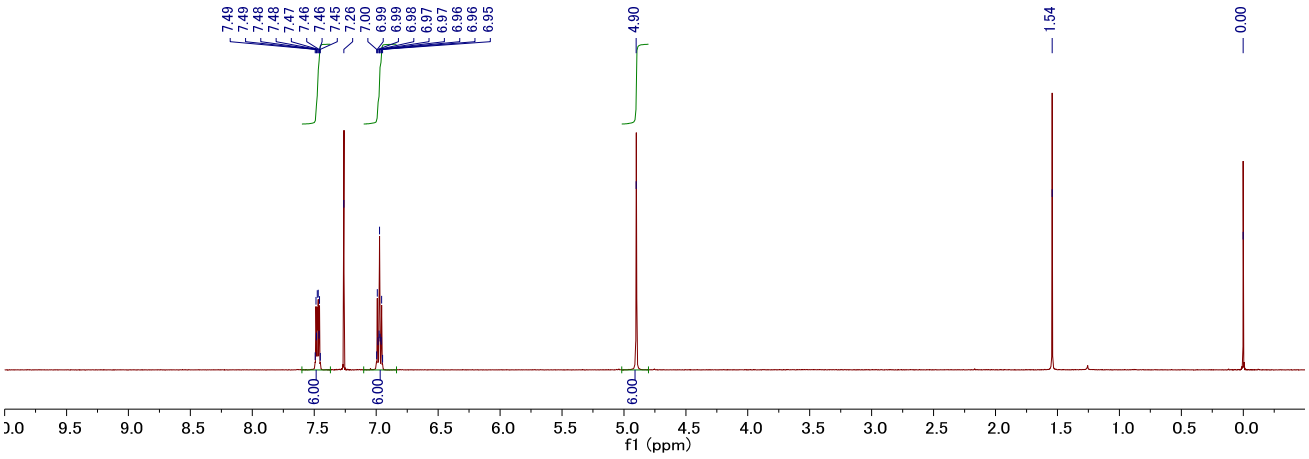


^{13}C-NMR spectra (125 MHz, $CDCl_3$, Me_4Si) of compound **1**





^{1}H-NMR spectra (500 MHz, $CDCl_3$, Me_4Si) of compound **2**



^{13}C-NMR spectra (125 MHz, $CDCl_3$, Me_4Si) of compound **2**