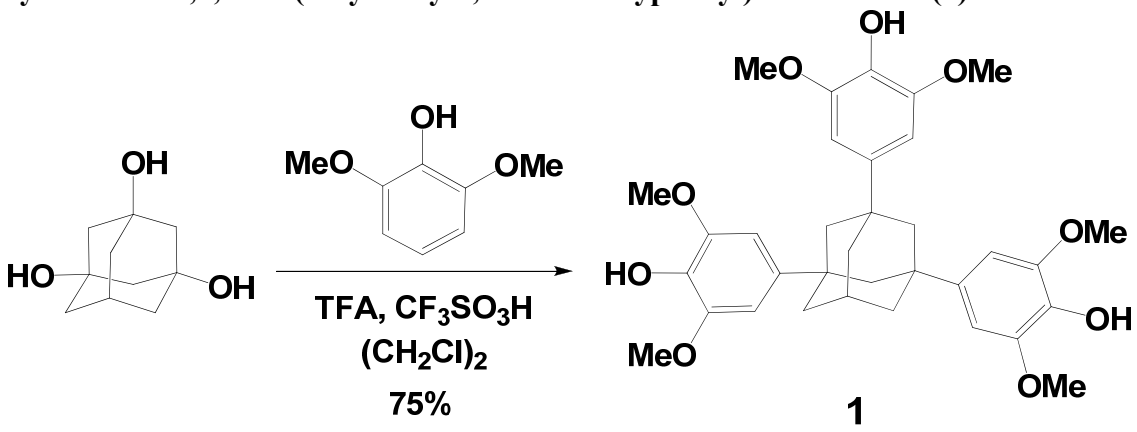
Supporting Information

Hydrogen-bonded networks formed from tri- and tetrasubstituted adamantanes bearing dimethoxyphenol moieties and their 1,3,5-trinitrobenzene complexes via charge-transfer interaction

Masahide Tominaga,* Kosuke Katagiri, Hyuma Masu, Isao Azumaya*

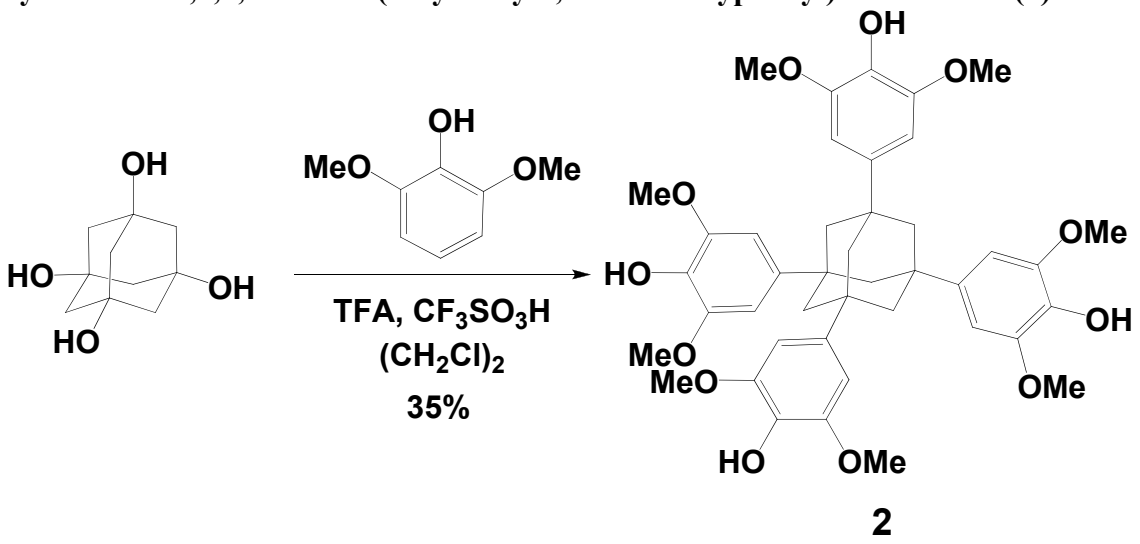
Synthesis of 1,3,5-tris(4-hydroxy-3,5-dimethoxyphenyl)adamantane (1)



A mixture of 1,3,5-adamantanetriol (3.31 g, 18.0 mmol) and 2,6-dimethoxyphenol (21.14 g, 81.0 mmol) in trifluoroacetic acid (100 mL) and 1,2-dichloroethane (100 mL) in the presence of catalytic amounts of trifluoromethansulfonic acid was stirred at 90 °C for 12 h under an argon atmosphere. The solvents were removed under reduced pressure and the reaction mixture was washed with H_2O, satureted aqueous $NaHCO_3$, H_2O, brine and dried over Na_2SO_4. The evaporation of the solvent was followed by silica gel column chromatography (eluent: $CHCl_3$) to afford the title compound as a white solid (8.00 g, 13.5 mmol) with a yield 75%. m.p. 220–221 ˚C. FT-IR (ATR, cm^{-1}): 3498, 2929, 1604, 1517, 1408, 1211, 1107, 794, 747. ^{1}H NMR (400 MHz, $CDCl_3$, 27 ˚C) δ 6.65 (s, 6H), 5.43 (s, 3H), 3.91 (s, 18H), 2.55 (s, 1H), 2.08–1.98 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ˚C) δ 146.77 (C_q–OCH_3), 141.39 (C_q), 133.15 (C_q–OH), 102.21

(*C*H), 56.46 (O−*C*H$_3$), 48.72 (*C*H$_2$), 41.66 (*C*H$_2$), 38.41 (C_q), 30.15 (*C*H). MS (FAB, *m/z*) Calcd for $C_{34}H_{41}O_9$ ($M+H^+$) 593.27, found 593.6. Elemental Analysis Calcd for $C_{34}H_{40}O_9$: C, 68.90; H, 6.80. Found: C, 68.63; H, 6.83.

Synthesis of 1,3,5,7-tetrakis(4-hydroxy-3,5-dimethoxyphenyl)adamantane (2)



A mixture of 1,3,5,7-adamantanetetraol (2.00 g, 10.0 mmol) and 2,6-dimethoxyphenol (12.32 g, 80.0 mmol) in trifluoroacetic acid (100 mL) and 1,2-dichloroethane (100 mL) in the presence of catalytic amounts of trifluoromethansulfonic acid was stirred at 90 °C for 12 h under an argon atmosphere. The solvents were removed under reduced pressure and the reaction mixture was washed with H_2O, satureted aqueous $NaHCO_3$, H_2O, brine and dried over Na_2SO_4. The evaporation of the solvent was followed by silica gel column chromatography (eluent: $CHCl_3$) to afford the title compound as a white solid (2.61 g, 3.50 mmol) with a yield 35%. m.p. 267–268 ˚C. FT-IR (ATR, cm^{-1}): 3478, 2920, 1611, 1522, 1407, 1221, 1101, 788, 745. ^{1}H NMR (400 MHz, $CDCl_3$, 27 ˚C) δ 6.70 (s, 8H), 5.51 (s, 4H), 3.91 (s, 24H), 2.10 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ˚C) δ 146.86 (C_q−OCH_3), 140.64 (C_q), 133.47 (C_q−OH), 102.36 (*C*H), 56.54 (O−*C*H$_3$), 48.84 (*C*H$_2$), 39.32 (C_q). MS (FAB, *m/z*) Calcd for $C_{42}H_{49}O_{12}$ ($M+H^+$) 745.31, found 745.7. Elemental Analysis Calcd for $C_{42}H_{48}O_{12}\cdot 0.1CHCl_3$: C, 66.82; H, 6.41.

Found: C, 66.69; H, 6.56.

(1) F. M. Menger and V. A. Migulin, *J. Org. Chem.,* 1999, **64***,* 8916.

(2) C. –F. Huang, H. -F. Lee, S. -W. Kuo, H. Xu and F. -C. Changa, *Polymer,* 2004, **45**, 2261.

Fig. S1 ^{1}H NMR of **1**

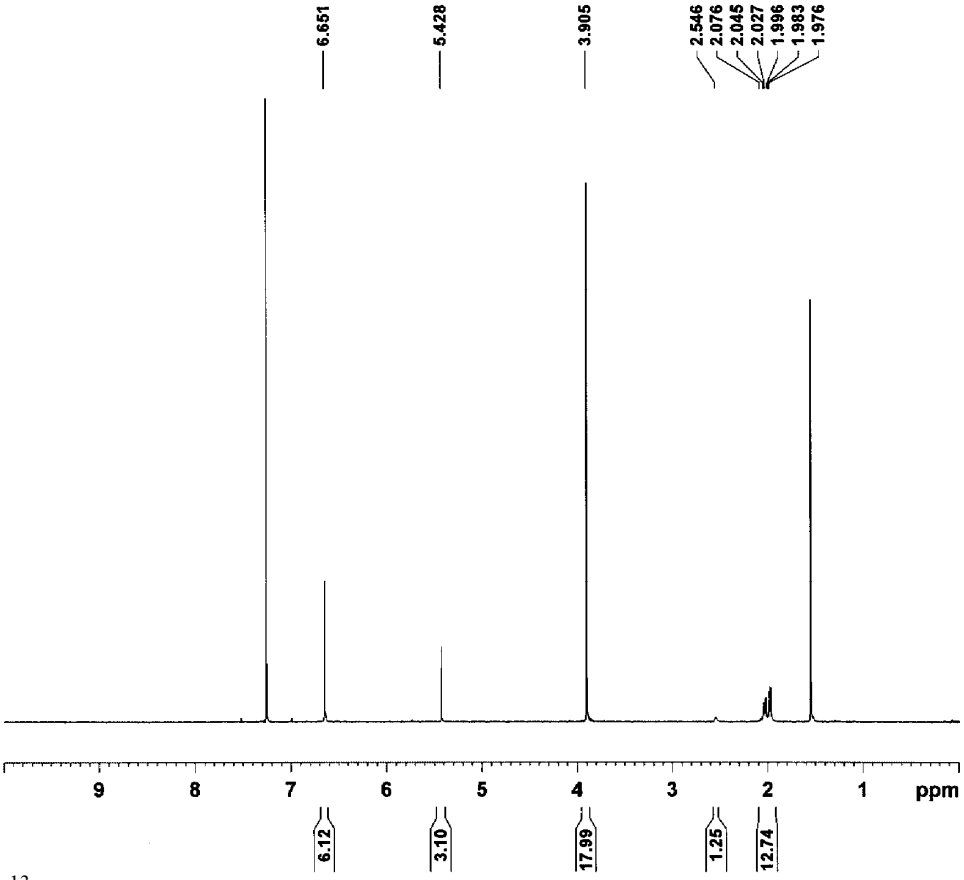


Fig. S2 ^{13}C NMR of **1**

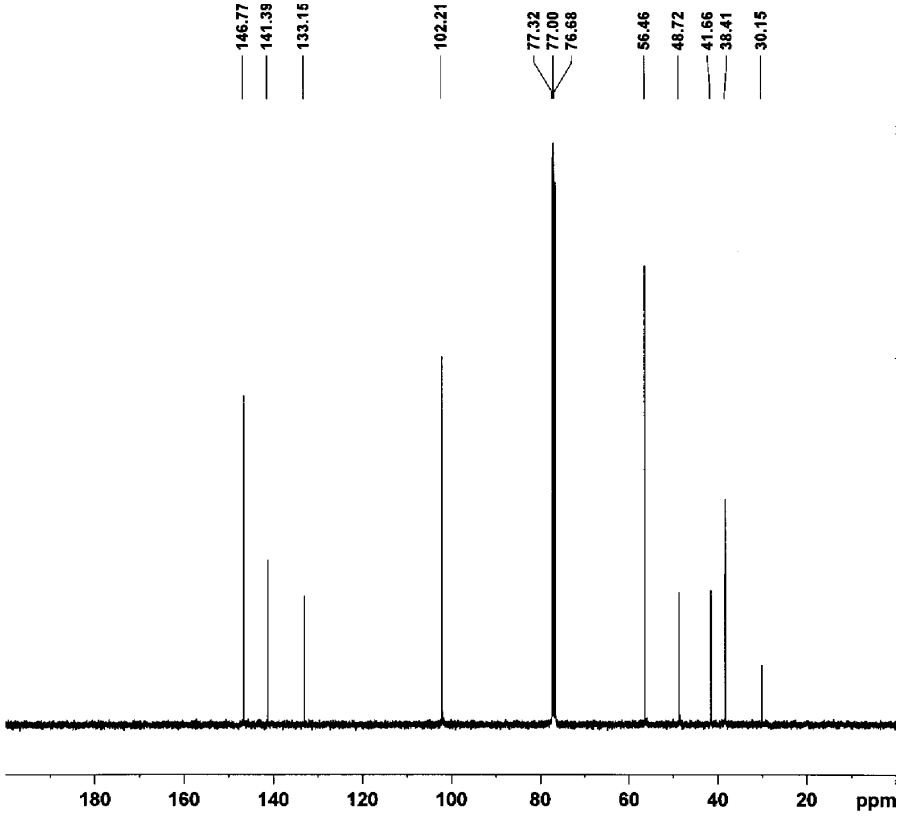


Fig. S3 ^{1}H NMR of **2**

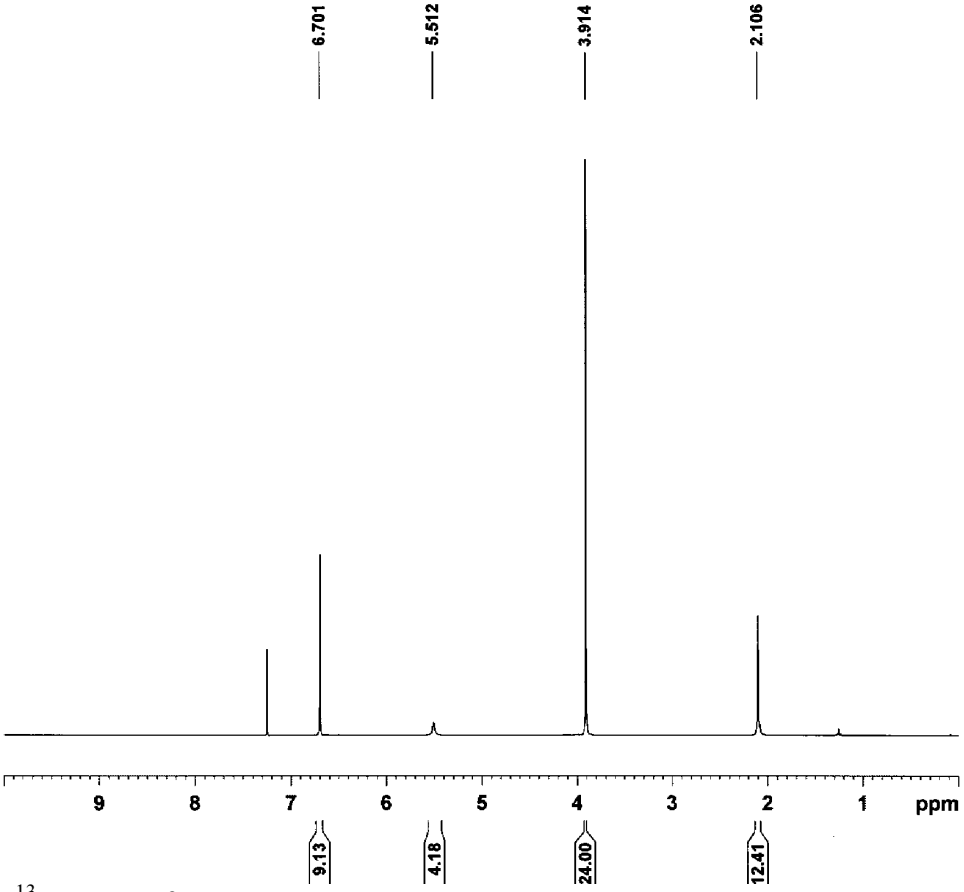
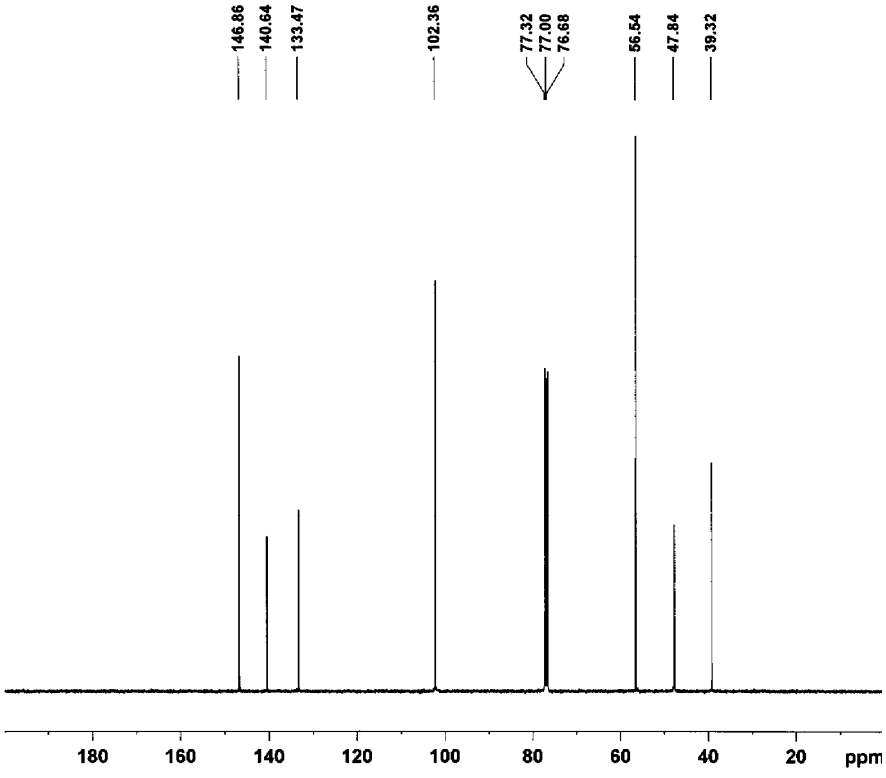


Fig. S4 ^{13}C NMR of **2**



X-ray Crystallographic Analysis

Crystal data for 1a: $C_{34}H_{40}O_9 \cdot 2CHCl_3$, M_r = 831.40, 0.45 × 0.40 × 0.35 mm, monoclinic, $P2_1/c$, a = 9.8585(6), b = 14.0448(8), c = 28.691(2) Å, β = 99.005(1)°, V = 3923.6(4) Å^3, Z = 4, D_c = 1.407 Mg m^{-3}, $2\theta_{max}$ = 54.40°, T = 120 K, 18927 reflections measured, 7914 unique (R_{int} = 0.0147). μ = 0.489 mm^{-1}, T_{max} = 0.8474, T_{min} = 0.8098, The final R_1 and $wR_2(F^2)$ was 0.0826 and 0.2495 ($I > 2\sigma(I)$), 0.0927 and 0.2585 (all data) for 488 parameters and 1 restraints. CCDC-740184.

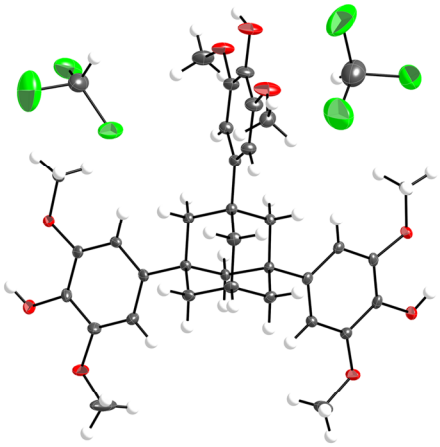


Fig. S5 Thermal ellipsoid model of crystal **1a**. The ellipsoids of non–hydrogen atoms are drawn at the 50% probability level.

Crystal data for 1b: $C_{40}H_{43}N_3O_{15}$, M_r = 805.77, 0.20 × 0.15 × 0.10 mm, monoclinic, $P2_1/c$, a = 10.066(1), b = 19.591(2), c = 19.371(2) Å, β = 98.623(1)°, V = 3777.0(7) Å^3, Z = 4, D_c = 1.417 Mg m^{-3}, $2\theta_{max}$ = 54.42°, T = 120 K, 18129 reflections measured, 7566 unique (R_{int} = 0.0275). μ = 0.109 mm^{-1}, T_{max} = 0.9891, T_{min} = 0.9784, The final R_1 and $wR_2(F^2)$ was 0.0403 and 0.0874 ($I > 2\sigma(I)$), 0.0733 and 0.1010 (all data) for 532 parameters. CCDC-740185.

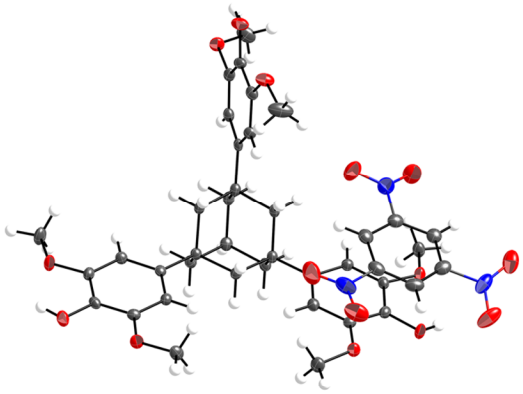


Fig. S6 Thermal ellipsoid model of crystal **1b**. The ellipsoids of non–hydrogen atoms are drawn at the 50% probability level.

Crystal data for 2a: $C_{42}H_{48}O_{12}\cdot 4CHCl_3$, M_r = 1222.28, 0.40 × 0.35 × 0.35 mm, monoclinic, *C*2/*c*, *a* = 31.279(3), *b* = 10.613(1), *c* = 22.276 (4) Å, β = 132.356(1)°, *V* = 5464.5(12) Å^3, *Z* = 4, D_c = 1.486 Mg m^{-3}, $2\theta_{max}$ = 54.26°, *T* = 120 K, 13020 reflections measured, 5515 unique (R_{int} = 0.0171). μ = 0.665 mm^{-1}, T_{max} = 0.8005, T_{min} = 0.7767, The final R_1 and $wR_2(F^2)$ was 0.0543 and 0.1370 ($I > 2\sigma(I)$), 0.0607 and 0.1421 (all data) for 323 parameters. CCDC-740186.

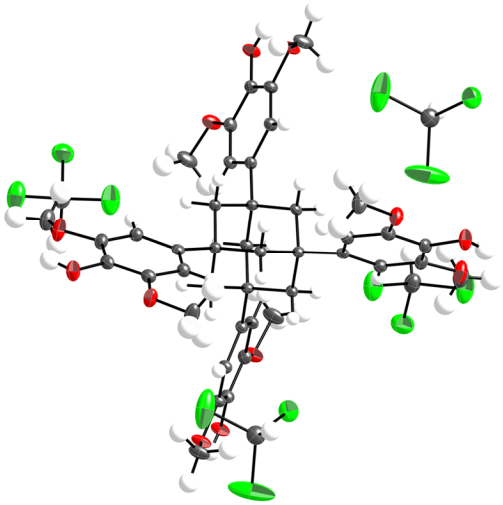


Fig. S7 Thermal ellipsoid model of crystal **2a**. The ellipsoids of non–hydrogen atoms are drawn at the 50% probability level.

Crystal data for 2b: $C_{42}H_{48}O_{12}\cdot 2C_6H_3N_3O_6\cdot CHCl_3$, *M*r = 1290.4, 0.35 × 0.30 × 0.05 mm, triclinic, *P*-1, a = 13.05(1), b = 14.34(2), c = 16.27(2) Å, α = 102.72(2), β = 91.78(1), γ= 107.30(1)°, V = 2821(5) Å^3, Z = 2, D_c = 1.519 Mg m^{-3}, $2\theta_{max}$ = 53.94°, T = 120 K, 13258 reflections measured, 10478 unique (R_{int} = 0.0460). μ = 0.251 mm^{-1}, T_{max} = 0.9874, T_{min} = 0.9160, The final R_1 and $wR_2(F^2)$ was 0.0785 and 0.2009 ($I > 2\sigma(I)$), 0.1627 and 0.2500 (all data) for 829 parameters. CCDC-740187.

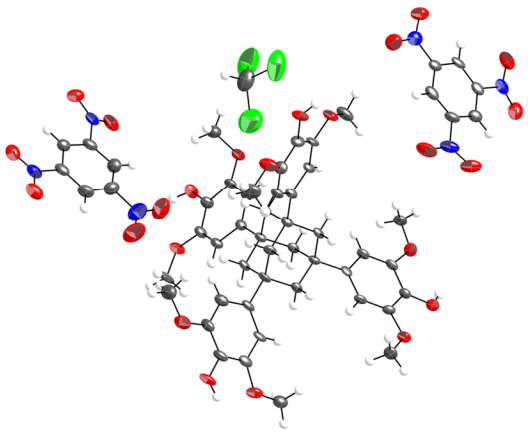


Fig. S8 Thermal ellipsoid model of crystal **2b**. The ellipsoids of non–hydrogen atoms are drawn at the 50% probability level.

Hydrogen bonds parameters

Table S1 Hydrogen bonds parameters for crystal **1a** and **1b**

1a		**1b**	
	Bond lengths (Å)		
O1–H1···O5’	2.919(3)	O1–H1···O6’	2.845(2)
O4–H4···O1’	2.836(3)	O4–H4···O2’	2.840(2)
	Bond angles (°)		
O1–H1–O5’	131.9	O1–H4–O6’	155.0
O1–H4–O1’	167.5	O4–H4–O2’	116.3

The position of hydrogen atoms was determined with constrains by SHELXL program.

Table S2 Hydrogen bonds parameters for crystal **2a** and **2b**

2a		**2b**	
	Bond lengths (Å)		
O1–H1···O6’	2.955(3)	O1–H1···O1’	2.945(7)
O4–H4···Cl10’	3.427(2)	O4–H4···O13’	3.259(6)
		O7–H7···O12’	2.683(5)
		O10–H10···O3’	2.874(5)
	Bond angles (°)		
O1–H1–O6’	140.7	O1–H1–O1’	145.0
O4–H4–Cl10	133.6	O4–H4–O13’	144.9
		O7–H7–O12’	144.9
		O10–H10–O3’	147.3

The position of hydrogen atoms was determined with constrains by SHELXL program.