Supplementary Information

Preparation and crystal structures of charge-transfer complexes of acyclic host molecules bearing pyrogallol derivatives with paraquat

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Table of Contents

Table S1 Geometrical parameters of 1 in crystal 1a and 1b.	
Table S2 Geometrical Parameters of 2 in crystal 2a and 2b.	S2
Fig. S1 The packing diagram of 1 in crystal 1a.	
Fig. S2 The packing diagram of 2 in crystal 2a.	S3
Fig. S3 ¹ H NMR spectra of 1.	
Fig. S4 ¹³ C NMR spectra of 1.	S4
Fig. S5 ¹ H NMR spectra of 2 .	
Fig. S6 13 C NMR spectra of 2.	S5
Fig. S7 Additional crystal data for 1a.	S6
Fig. S8 Additional crystal data for 1b.	S7
Fig. S9 Additional crystal data for 2a.	S 8
Fig. S10 Additional crystal data for 2b.	S9–10
Fig. S11 Hirshfeld Surfaces and 2D fingerprint plots of the 3^{2+} in crystal forms 1b.	
Fig. S12 Hirshfeld Surfaces and 2D fingerprint plots of the 3 ²⁺ in crystal forms 2b .	S11

P1 OMe MeO C ³ C ⁴ P2 OMe OMe OMe			
Crystal	1a	1b	
Torsion Angle (deg)			
$C^{1}-C^{2}-C^{3}-C^{4}$	-61.89	-65.86	
$C^{4}-C^{5}-C^{6}-C^{7}$	4.54	-58.21	
Dihedral Angle (deg) P1-P2	57.90	89.47	

Table S1 Geometrical parameters of 1 in crystal 1a and 1b.

Table S2 Geometrical parameters of 2 in crystal 2a and 2b.





Fig. S1 The packing diagram of 1 in crystal 1a. (a) Top and (b) side views of network structures. Solvent molecules have been omitted for charity.



Fig. S2 The packing diagram of **2** in crystal **2a**. (a) Top and (b) side views of network structures. Solvent molecules have been omitted for charity.





Additional crystal data for 1a

The colourless prismatic crystal ($0.250 \times 0.140 \times 0.100 \text{ mm}^3$), which was obtained from chloroform/methanol, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. The diffraction experiment was performed in a Bruker APEX II system (APEX II CCD detector, MoKa: $\lambda = 0.71073$ Å). Absorption correction was performed by an empirical method implemented in SADABS.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2016/6³.

 $C_{29}H_{37}Cl_{3}O_{6}$, Mr = 587.93; monoclinic, space group $P2_{1}/c$, Z = 4, $D_{calc} = 1.372$ g·cm⁻³, a = 17.6945(11), b = 11.4264(7), c = 14.1947(9) Å, $\beta = 97.3820(10)^{\circ}$, V = 2846.2(3) Å³, 25518 observed and 4573 independent $[I > 2\sigma(I)]$ reflections, 349 parameters, final $R_{1} = 0.0336$, $wR_{2} = 0.0814$, S = 1.057 $[I > 2\sigma(I)]$. CCDC 1575309

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms.



Fig. S7 Ortep drawing of crystal 1a (50% probability).

Additional crystal data for 1b

The reddish brown block crystal $(0.100 \times 0.050 \times 0.020 \text{ mm}^3)$, which was obtained from acetone, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuK α : $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2016/6³.

 $C_{34}H_{43}F_6NO_6P$, Mr = 706.66; triclinic, space group P-1, Z = 2, $D_{calc} = 1.423$ g·cm⁻³, a = 9.6564(11), b = 13.3543(15), c = 14.3477(16) Å, $\alpha = 67.011(4)^\circ$, $\beta = 76.108(4)^\circ$, $\gamma = 80.955(4)^\circ$, V = 1649.3(3) Å³, 19948 observed and 5780 independent $[I > 2\sigma(I)]$ reflections, 441 parameters, final $R_1 = 0.0613$, $wR_2 = 0.2033$, S = 1.132 $[I > 2\sigma(I)]$. CCDC 1575310

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with $U_{\rm iso}$ values constrained to 1.2/1.5 $U_{\rm eq}$ of their parent atoms.



Fig. S8 Ortep drawing of crystal 1b (50% probability).

Additional crystal data for 2a.

The colourless prismatic crystal ($0.200 \times 0.150 \times 0.070 \text{ mm}^3$), which was obtained from acetone/ethanol, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuK α : $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2016/6³.

 $C_{37.84}H_{49}O_{9.66}$, Mr = 658.41; triclinic, space group *P*-1, Z = 2, $D_{calc} = 1.239$ g·cm⁻³, a = 10.1729(16), b = 13.993(2), c = 14.345(2) Å, a = 63.733(4), $\beta = 84.981(4)$, $\gamma = 74.713(4)^{\circ}$, V = 1765.3(5) Å³, 21711 observed and 6572 independent [$I > 2\sigma(I)$] reflections, 472 parameters, final $R_1 = 0.0421$, $wR_2 = 0.1197$, S = 1.069 [$I > 2\sigma(I)$]. CCDC 1575311

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water were found by the Fourier map and refined isotropically. Another hydrogen atoms were also refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The ethanol molecule riding on a symmetry center was refined with PART -n. The occupancies of ethanol and water were refined by free variables to be ca. 42% and ca. 23% respectively.



Fig. S9 Ortep drawing of crystal 2a (50% probability).

Additional crystal data for 2b.

Repeated recrystallization and data collection were attempted to represent the best of all. The weakly diffracting reddish brown block crystal ($0.110 \times 0.050 \times 0.020 \text{ mm}^3$), which was obtained from acetone, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuK α : $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2016/6³.

 $C_{45.31}H_{57.63}F_6NO_{9.77}P$, Mr = 917.62; triclinic, space group P-1, Z = 2, $D_{calc} = 1.385$ g·cm⁻³, a = 9.6535(16), b = 12.475(2), c = 18.922(3) Å, $\alpha = 83.815(6)^\circ$, $\beta = 84.842(6)^\circ$, $\gamma = 76.722(6)^\circ$, V = 2199.9(6) Å³, 28079 observed and 7306 independent $[I > 2\sigma(I)]$ reflections, 610 parameters, final $R_1 = 0.0434$, $wR_2 = 0.1265$, S = 1.140 $[I > 2\sigma(I)]$. CCDC 1575312

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. A pair of disordered methoxy moieties were refined as part A (C36A and O8A) and part B (C36B and O8B). The occupancy ratio of A vs. B was ca. 65/35. The crystal contained one solvent acetone molecule, and the occupancy was ca. 77%.



Fig. S10 Ortep drawing of crystal 2b (50% probability).

- (1) G. M. Sheldrick, (1996). SADABS. University of Göttingen, Germany.
- (2) G. M. Sheldrick, Acta. Cryst., 2015, A71, 3-8.
- (3) G. M. Sheldrick, Acta. Cryst., 2015, C71, 3-8.



Fig. S11 Hirshfeld Surfaces and 2D fingerprint plots of the 3^{2+} in crystal forms 1b.



Fig. S12 Hirshfeld Surfaces and 2D fingerprint plots of the 3^{2+} in crystal forms 2b.