Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

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Experimental details

Measurements

IR spectra were measured by a JASCO FT/IR-420 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer (400 MHz for ^{1}H) for samples dissolved in deuterated methanol. The ultraviolet-visible (UV-Vis) absorption spectra of the solid samples were acquired using a conventional optical microscope equipped with an optical fiber connected to a spectrometer (Ocean Optics USB4000) and a temperature-controlled stage (Linkam THMS600). The incident light was guided from a high-pressure Hg lamp via a 330–380 nm bandpass filter. The samples were prepared by depositing thin-plate crystals obtained by solution recrystallization on a glass slide. The spectra was captured with an acquisition time of 100 ms, and averaged over 10 runs (namely, the total acquisition time of 1.0 s). To capture the spectra of photospecies, the sample was irradiated with an Hg lamp through a dichroic mirror cube, and after the spectral change was saturated the dichroic mirror cube was replaced with a half-mirror cube that intercepts the UV irradiation.

Materials

Apo-hosts **1** and **2** were prepared in accordance with the literature (A. C. Soegiarto, et al., *J. Am. Chem. Soc.*, 2010, 132, 14603.; A. C. Soegiarto and M. D. Ward, *Cryst. Growth Des.*, 2009, 9, 3803.), using Guanidinium carbonate, biphenyl-4,4′-disulfonic acid (for **1**) or naphthalene-2,6-disulfonic acid disodium salt (for **2**). The sodium salt was acidified with Amberlyst 36 (wet) ion-exchange resin. Guanidinium carbonate was treated with tetrafluoroboric acid to exchange its counter anion, and then mixed with the sulfonic acid. Salicylideneaniline and 3,5-di-*tert*-butyl-salicylidene-3-nitroaniline were prepared by condensation reaction in methanol solution. All the chemicals were purchased from TCI or FUJIFILM Wako, and used without further purification.

SA@1: The apo-host **1** of 74.2 mg (0.086 mmol for $(CH_6N_3)_4(C_{12}H_8O_6S_2)_2$ unit) and SA of 88.8 mg (0.45 mmol) was dissolved together in methanol (10 mL). Every 1 mL of the solution was moved to a polypropylene micro test tube, which was left loosely capped. After a week the precipitates were collected with a membrane filter and washed with acetone. Drying under reduced pressure for 6h yielded yellow needles of 29.3 mg (32%). ^{1}H NMR (400 MHz : CD_3OD): δ = 6.96 (m, 2H, Ar-H), 7.3-7.5 (m, 6H, Ar-H), 7.73 (d, 4H, *J* = 8.0 Hz, Ar-H), 7.91 (d, 4H, *J* = 8.0 Hz , Ar-H), 7.52 (d, 1H, Ar-H), 8.80 (s, 1H, -CH=N-) ppm, ^{13}C NMR (100 MHz : CD_3OD): δ = 116, 118, 119, 120, 126, 127, 128, 129, 132, 132, 143, 145, 149, 160, 161, 163 ppm.

SA@2: The apo-host **2** of 61.0 mg (0.075 mmol for $(CH_6N_3)_4(C_{10}H_6O_6S_2)_2$ unit) and SA of 88.8 mg (0.45 mmol) was dissolved together in methanol (10 mL). Every 1 mL of the solution was moved to a polypropylene micro test tube, which was left loosely capped. After a week the precipitates were collected with a membrane filter and washed with acetone. Drying under reduced pressure for 6h yielded yellow needles of 32.7 mg (43%). ^{1}H NMR (400 MHz: CD_3OD):δ = 6.96 (m, 2H, Ar-H), 7.3-7.5 (m, 6H, Ar-H), 7.52 (d, 1H, Ar-H), 7.94 (dd, 2H, *J* =7.0 Hz, 1.5 Hz, Ar-H), 8.03 (d, 2H, *J* = 8.0 Hz, Ar-H), 8.39 (d, 2H, *J* = 1.5 Hz, Ar-H), 8.80 (s, 1H, -CH=N-) ppm, ^{13}C NMR (100 MHz: CD_3OD): δ = 116, 118, 119, 120, 125, 126, 126, 129, 130, 132, 132, 134, 145,149, 160, 161, 163 ppm.

Crystallography

For X-ray diffraction of single crystals, data were collected on a Rigaku XtaLAB P200, λ (Mo-K_α) = 0.71075 Å. The structures were solved by direct method (SHELXS-2013) (G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, 64, 112.) and refined on F^2 by full-matrix least-square techniques (SHELXL-2018). (G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, 71, 3.) Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-2062419 and 2062420 for SA@1 and SA@2.

SA@1: Pale yellow plate recrystallized with methanol. $C_{41}H_{51}N_{13}O_{13}S_4$, Mw =1062.18, triclinic, a = 7.1866(2), b= 12.4312(3), c = 13.8896(5) Å, α = 93.039(2), β = 96.532(3), γ = 93.712(2)°, V = 1227.94(6) Å^3, D_{calcd} = 1.436 g/cm3, T = 93 K, space group P-1 (#2), Z = 1, λ(Mo-K_α) = 2.69 cm^{-1}, 34869 reflections measured and 5977 unique ($2\theta_{\text{max}}$ = 58.6˚, R_{int} = 0.0469) which were used in all calculations. R = 0.0655, R_{w} = 0.1864.

SA@2: Pale yellow prism recrystallized with methanol. $C_{37}H_{47}N_{13}O_{13}S_4$, Mw = 1010.11, triclinic, a = 7.12180(10), b = 12.5455(3), c = 13.6688(3) Å, α = 113.601(2), β = 99.3307(15), γ = 91.6841(16)°, V = 1098.28(4) Å^3, D_{calcd} = 1.527 g/cm3, T = 93 K, space group P-1 (#2), Z = 1, λ(Mo-K_α) = 2.97 cm^{-1}, 30899 reflections measured and 5282 unique ($2\theta_{\text{max}}$ = 58.1˚, R_{int} = 0.0259) which were used in all calculations. R = 0.0482, R_{w} = 0.1517.

Supplementary figures

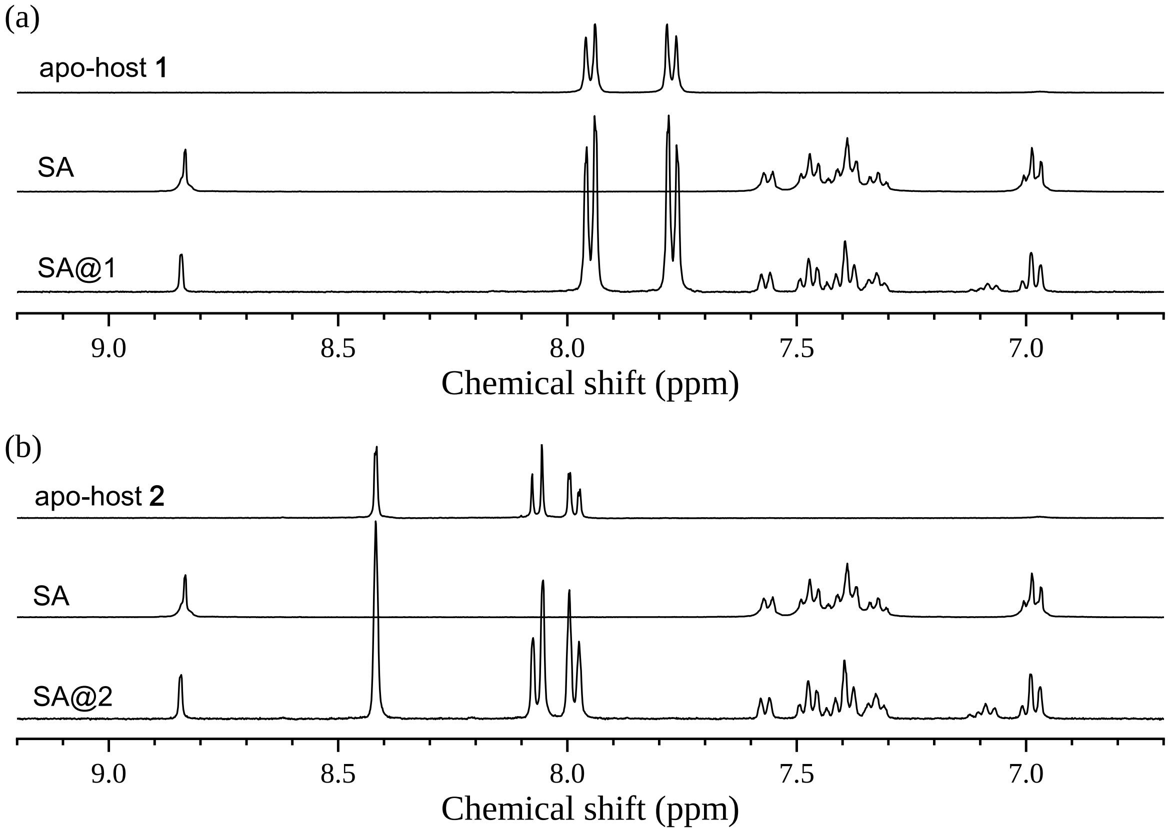

Figure S1 ^{1}H NMR spectra of (a) SA@1 and (b) SA@2 as compared with the apo-hosts **1** and **2**, and pure SA. The ratio of SA to biphenyl-4,4′-disulfonic acid was 0.89 : 2 for SA@1, and that to naphthalene-2,6-sulfonic acid was 0.82 : 2 for SA@2.

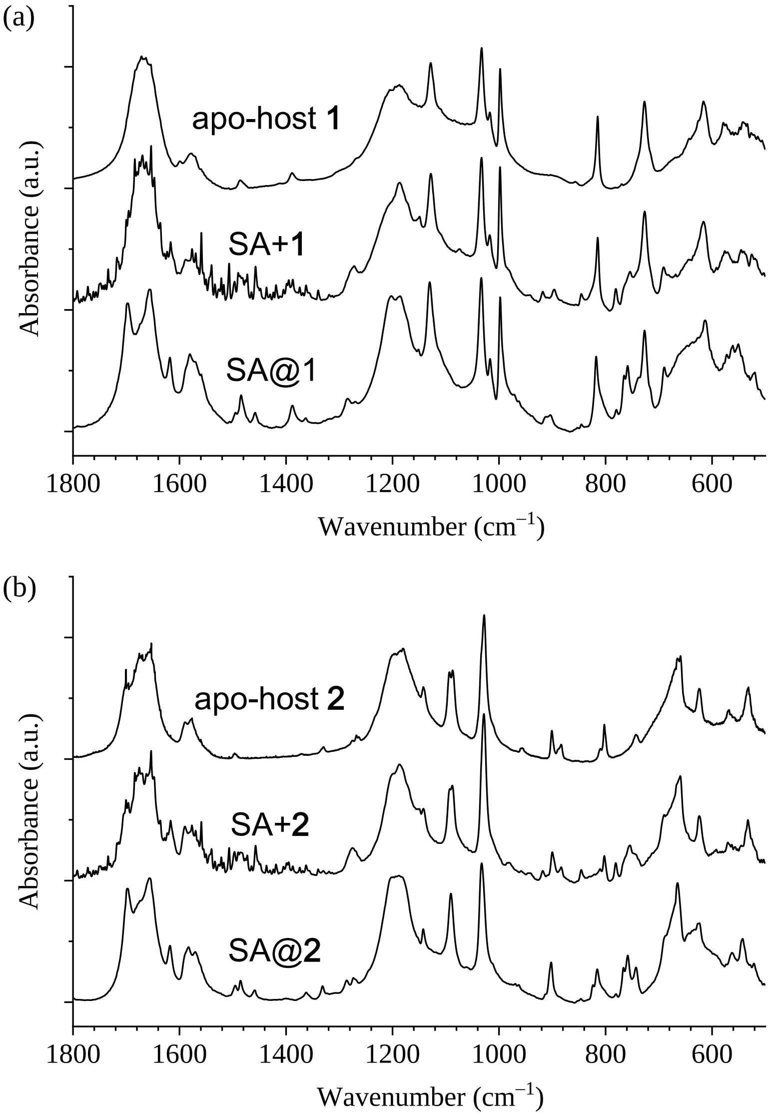

Figure S2 FT-IR spectra of (a) SA@1 and SA@2 as compared with the apo-hosts **1** and **2**. Spectra of the 1:1 physical mixtures of SA and **1** or **2**, denoted as SA+1 and SA+2, respectively, are included.

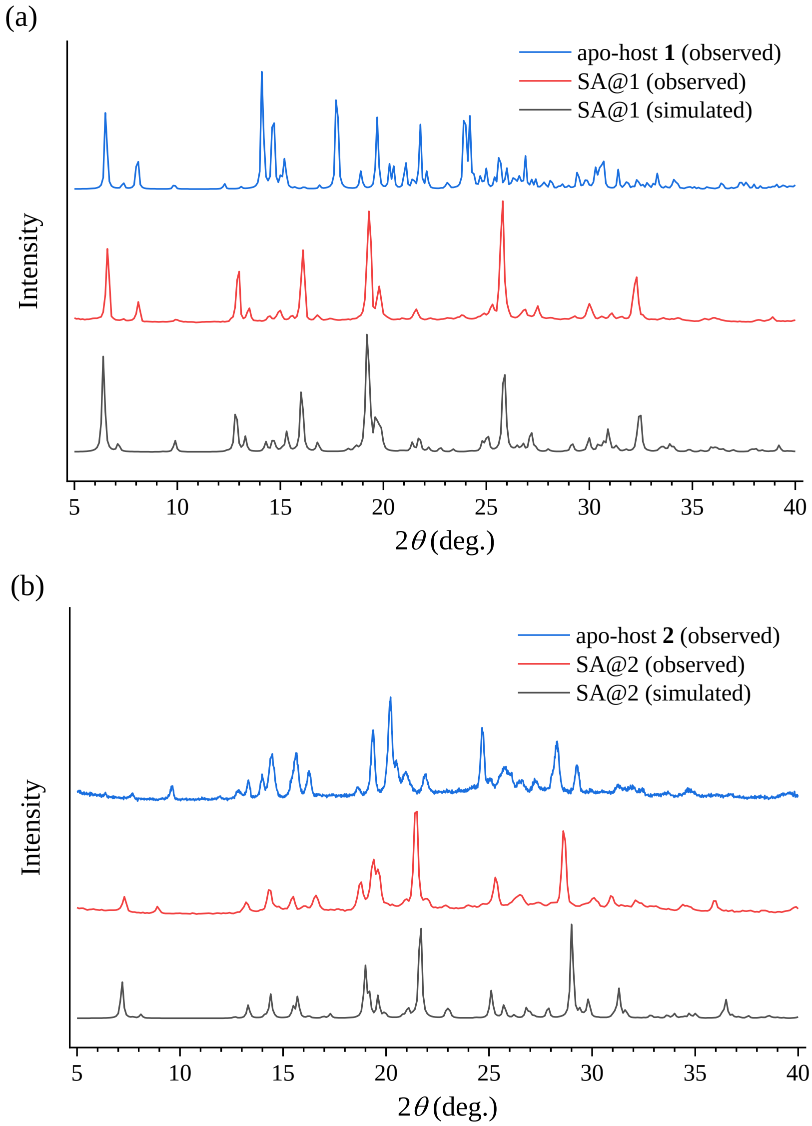

Figure S3 Powder XRD patterns observed for (a) SA@1 and (b) SA@2, together with their simmulated patterns based on the single-crystal structures. The XRD patterns of the apo-hosts **1** and **2** are included. For the preferred orientation in clathrates, a March-Dollase factors (1.5 to the SA@1 (0 0 1) plane and 0.7 to the SA@2 (0 0 1) plane) were applied (W.A. Dollase, *J. Appl. Cryst.* 1986, 19, 267.) unsing Mercury software (C. F. Macrae, et al., *J. Appl. Cryst.*, 2020, 53, 226.).

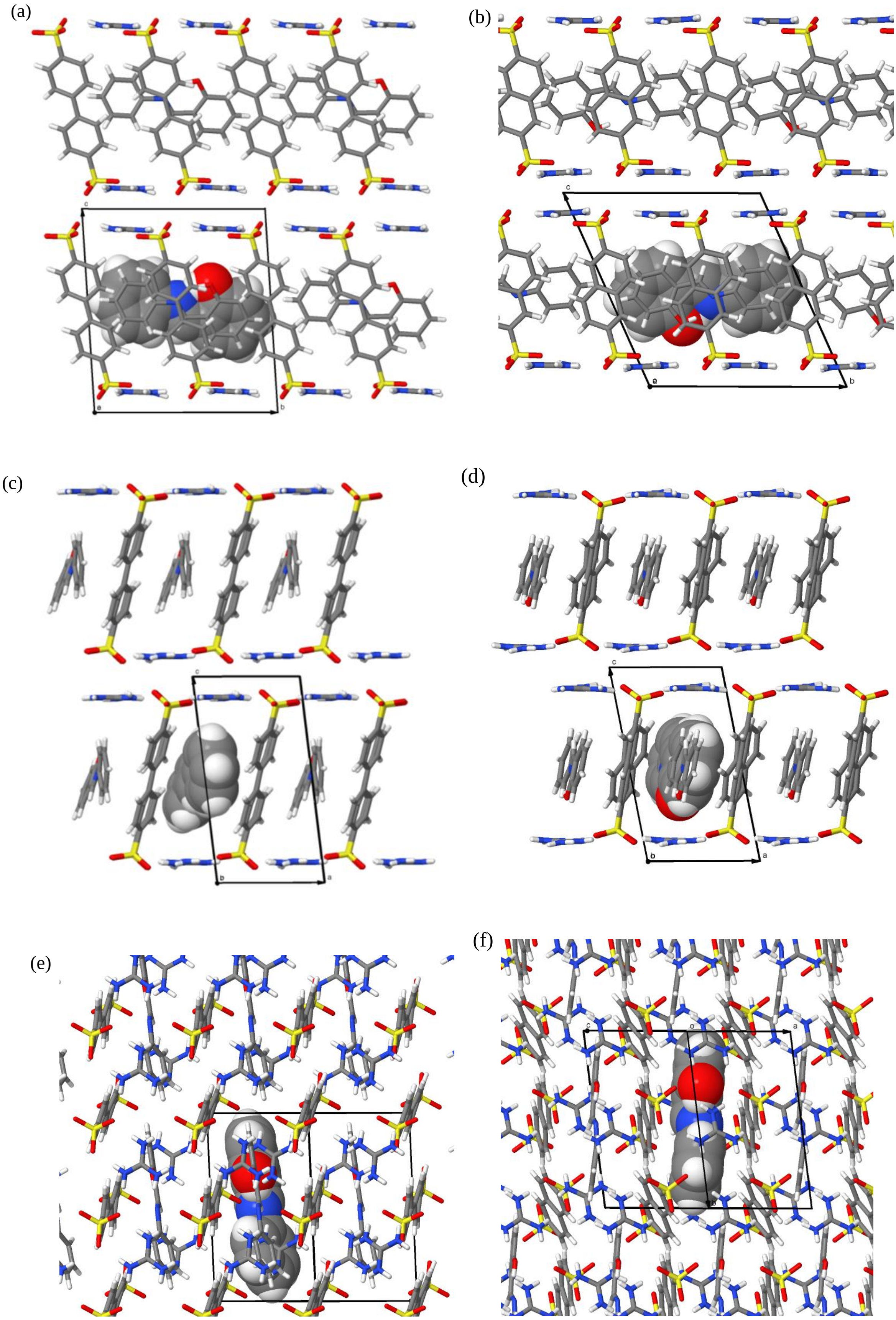

Figure S4 Comparison of the crystal structures of SA@1 (a, c, e) and SA@2 (b, d, f). (a,b) views from *a*-axis; (c, d) views from *b*-axis; (e, f) views from *a*+*c* orientation.

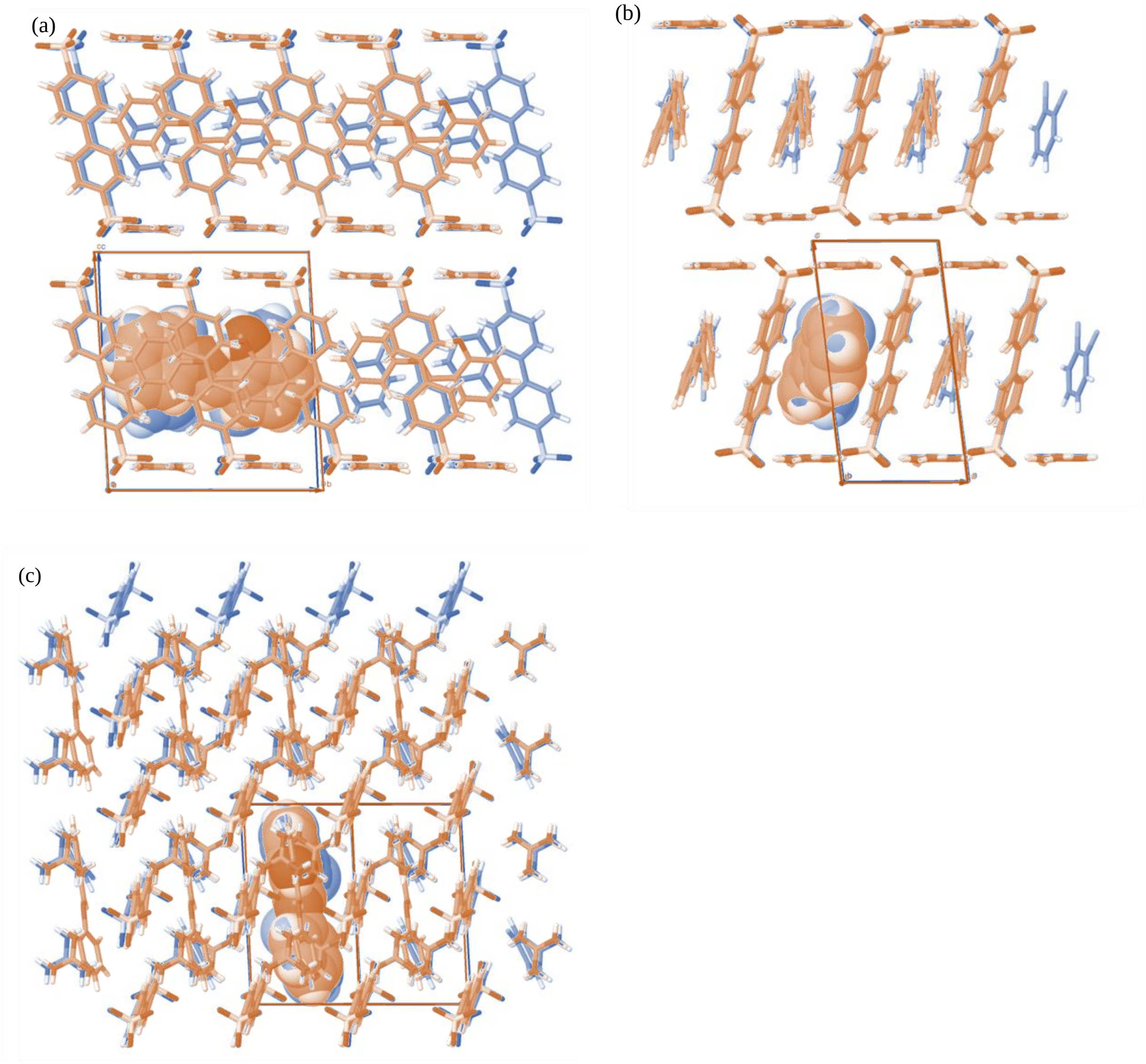

Figure S5 Comparison of the crystal structures of SA@1 (orange) and *o*-dichlorobenzene clathrate of **1** (CCDC refcode XAQWUH) (blue). For the biphenyl moieties in SA@1, one of the four possible orientations are shown. (a) from *a*-axis, (b) from *b*-axis, (c) from *a*+*c* orientation.