Electronic Supplementary Information

Photoinduced electron transfer in porous organic salt crystals impregnated with fullerenes

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Experimental section

Synthesis of 9-(4-sulfophenyl)anthracene: A solution of 1,4-dioxane (150 mL) containing anthracene (13.2 g, 74.2 mmol) and sulfanylamide (4.33 g, 25.1 mmol) was heated to 80 ºC and mixed with isoamyl nitrite (5.00 mL, 37.2 mmol) slowly under stirring. The reaction mixture was refluxed for 1.5 h at 80 ºC. The reaction mixture was cooled to room temperature and then evaporated to remove the solvent *in vacuo*. After washing by distilled water, the residue was purified by silica column chromatography (CH_2Cl_2/EtOAc = 19/1). The resulting powder was washed by a small amount of 1,4-dioxane to give 9-(4-sulfonamidephenyl)-anthracene (9-SAPA, 1.34 g, 4.01 mmol, 16%) as a yellow white solid. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.74 (s, 1H,), 8.19 (d, J = 8.8 Hz 2H,), 8.08 (d, J = 8.0 Hz, 2H,), 7.64 (d, J = 7.6 Hz, 2H,), 7.55(m, 4H,), 7.47 (d, J =3.6 Hz, 4H,).

A 1,4-dioxane solution (80 mL) containing 9-SAPA (1.00 g, 3.00 mmol) was heated to 110 ºC and mixed with isoamyl nitrite (1.00 mL, 7.44 mmol) slowly under stirring. The reaction mixture was refluxed for 45 min at 110 ºC, cooled to room temperature and then distilled to remove the solvent *in vacuo*. The residue was added water, and neutralized with $NaHCO_3$. Mixing with sodium chloride saturated water precipitates yellow white solid.

The solid dried *in vacuo*, and was washed by ether to give a sodium salt of 9-SPA (9-SPANa, 0.900 g, 25.3 mmol, 84%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.69 (s, 1H,), 8.16 (d, J =8.8 Hz 2H,), 7.85 (d, J =8.4 Hz, 2H,), 7.54 (m, 4H,), 7.44 (d, J =7.2 Hz 2H,), 7.36 (d, J = 8.4 Hz, 2H,). 9-SPA was obtained from ion-exchanging of 9-SPANa.

Preparation of the organic salt composed of 9-SPA and TPMA:

9-SPA was mixed with equimole of triphenylmethylamine (TPMA) in water. The solution was evaporated to yield yellow powder of the crude salt.

Transient absorption measurements: Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (λ = 786 nm, 2 μJ/pulse and fwhm =

130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into a second harmonic generation (SHG) unit: Apollo (Ultrafast Systems) for excitation light generation at λ = 393 nm, while the rest of the output was used for white light generation. The laser pulse was focused on a sapphire plate of 3 mm thickness and then white light continuum covering the visible region from λ = 410 nm to 800 nm was generated via self-phase modulation. A variable neutral density filter, an optical aperture, and a pair of polarizer were inserted in the path in order to generate stable white light continuum. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at λ = 393 nm of SHG output was irradiated at the sample cell with a spot size of 1 mm diameter where it was merged with the white probe pulse in a close angle ($< 10^{\circ}$). The probe beam after passing through the 2 mm sample cell was focused on a fiber optic cable that was connected to a CMOS spectrograph for recording the time-resolved spectra (λ = 410 - 800 nm). Typically, 3000 excitation pulses were averaged for 3 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were performed by using a potassium bromide disk pellets containing 9-SPA/TPMA/fullerene. The pellets were prepared by grinding the KBr powder and the 9-SPA/TPMA/fullerene crystals by pestle and mortar.

ESR measurements: A quartz ESR tube (internal diameter: 4.5 mm) containing 9-SPA/TPMA/fullerene crystals was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000-W high-pressure Hg lamp (Ushio-USH1005D) through an aqueous filter at low temperature. ESR spectra were measured under non-saturating microwave power conditions using a JEOL X-band spectrometer (JES-RE1XE) with an attached variable temperature apparatus. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra when the maximum slope linewidth (ΔH_{msl}) of the ESR signals was unchanged with a larger modulation magnitude. The *g* values and the zero-filed splitting values were calibrated with a Mn^{2+} marker.

Determination of single-crystal structures by X-ray crystallography:

SPA/TPMA was recrystallized from *o*-dichlorobenzene/*n*-hexane to give single crystals suitable for X-ray single crystallographic analysis. Diffraction data were collected by using the synchrotron radiation (λ = 0.75000 Å) at the BL26B1 in the SPring-8 with approval of JASRI (2014B1976). The cell refinements were performed with HKL2000 software. (1) Direct method (SIR-2004) was used for the structure solution.(2) Calculation was performed with the observed reflections [$I > 2\sigma(I)$] with the program CrystalStructure crystallographic software packages,(3) except for refinement, which was performed using SHELXL Version 2014/7.(4) All non-hydrogen atoms was refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. $C_{39}H_{31}NO_3S$, M_w = 593.74, a = 25.9455(3), b = 25.9455(3), c = 24.2457(2) Å, α = 90°, β = 90°, γ = 90°, V = 16321.5(3) $Å^3$, T = 153 K, tetragonal, space group *P*4/ncc (#130), Z = 4, ρ_{calcd} = 0.966 g cm^{-3}, 6314 unique reflections, the final *R*1 and *wR*2 values 0.0603 ($I > 2.0\sigma(I)$) and 0.1965 (all data), respectively. Crystallographic data for this paper has been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 1044710.

SPA/TPMA/C_{60} was recrystallized from *o*-dichlorobenzene/*n*-hexane solution of C_{60} to give single crystals suitable for X-ray single crystallographic analysis. Diffraction data were collected by using the synchrotron radiation (λ = 0.8000 Å) at the BL38B1 in the SPring-8 with approval of JASRI (2013B1245). The cell refinements were performed with HKL2000 software.(1) Direct method (Superflip) was used for the structure solution.(5) Calculation was performed with the observed reflections [$I > 2\sigma(I)$] with the program CrystalStructure crystallographic software packages,(3) except for refinement, which was performed using SHELXL Version 2014/7. (4) All non-hydrogen atoms was refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters.

$C_{60}H_{45}NO_3S$, M_w = 860.03, a = 26.77470(10), b = 26.77470(10), c = 24.07250(10) Å, α = 90°, β = 90°, γ = 90°, V = 17257.20(12) Å^3, T = 153 K, tetragonal, space group $P$4/ncc (#130), Z = 16, ρ_{calcd} = 1.324 g cm^{-3}, 10678 unique reflections, the final $R1$ and $wR2$ values 0.1138 ($I > 2.0\sigma(I)$) and 0.3735 (all data), respectively. Crystallographic data for this paper has been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 1044711.

SPA/TPMA/C$_{70}$ was recrystallized from toluene/*n*-hexane solution of C70 to give single crystals suitable for X-ray single crystallographic analysis. Diffraction data were collected by using the synchrotron radiation (λ = 0.8000 Å) at the BL38B1 in the SPring-8 with approval of JASRI (2013B1245). The cell refinements were performed with HKL2000 software. (1) Direct method (SIR-2008) was used for the structure solution.(6) Calculation was performed with the observed reflections [$I > 2\sigma(I)$] with the program CrystalStructure crystallographic software packages,(3) except for refinement, which was performed using SHELXL Version 2014/7.(4) All non-hydrogen atoms was refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters.

$C_{62.5}H_{45}NO_3S$, M_w = 890.055, a = 27.3864 (10), b = 27.3864 (10), c = 24.2386(5) Å, α = 90°, β = 90°, γ = 90°, V = 18179.3(10) Å^3, T = 153 K, tetragonal, space group $P$4/ncc (#130), Z = 16, ρ_{calcd} = 1.301 g cm^{-3}, 7071 unique reflections, the final $R1$ and $wR2$ values 0.1293 ($I > 2.0\sigma(I)$) and 0.4357 (all data), respectively. Crystallographic data for this paper has been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 1044712.

Note: Each guest molecule was highly disordered, therefore the data for DCB and C70 collected even in a synchrotron radiation facility were not effectively improved.

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(3) CrystalStructure ver 4.1, Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan.

(4) G. M. Sheldrick, *Acta Crystallogr.*, *A*, 2008, **64**, 112-122.

(5) L. Palatinus and G. Chapuis, *J. Appl. Cryst.,* 2007, **40**, 786-790.

(6) M. C, Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi and R. Spagna, *J. Appl. Cryst.,* 2007, **40**, 609-613.

Table S1 X-ray crystallographic parameters for the crystals.

compound	SPA/TPMA/ *o*-dichlorobenzene a)	SPA/TPMA/ C_{60}	SPA/TPMA/ C_{70}
Formula	$C_{39}H_{31}NO_3S$ a)	$C_{60}H_{45}NO_3S$	$C_{62.5}H_{45}NO_3S$
Mw	593.74	860.03	890.055
Crystal system	tetragonal	tetragonal	tetragonal
Space group	*P*4/ncc (#130)	*P*4/ncc (#130)	*P*4/ncc (#130)
Radiation wavelength	0.75000	0.80000	0.80000
Radiation type	synchrotron	synchrotron	synchrotron
Temperature (K)	153	153	153
a (Å)	25.9455(3)	26.77470(10)	27.3864(10)
b (Å)	25.9455(3)	26.77470(10)	27.3864(10)
c (Å)	24.2457(2)	24.07250(10)	24.2386(5)
α	90°	90°	90°
β	90°	90°	90°
γ	90°	90°	90°
V (Å^3)	16321.5(3)	17257.20(12)	18179.3(10)
Z	16	16	16
D_x (g cm^{-3})	0.966	1.324	1.301
No. of obs.	87845	147404	79696
No. of uniq.	6314	10678	7071
No. of parameters	398	993	1082
θ_{max} (°)	27.25	32.23	28.75
$R[F^2 > 2\theta(F^2)]$,	0.0603	0.1138	0.1293
$wR(F^2)$	0.1965	0.3735	0.4357
S	1.084	1.580	1.190
CCDC no.	1044710	1044711	1044712

a) Attempts to refine peaks of residual electron density as guest atoms were unsuccessful, although this crystal included *o*-dichlorobenzene. The data were corrected for disordered electron density through use of the SQUEEZE procedure. As a result of thermogravimetric analysis, host-guest ratio is ca. 1:1.1 ($C_{39}H_{31}NO_3S$•$1.1C_6H_4Cl_2$).

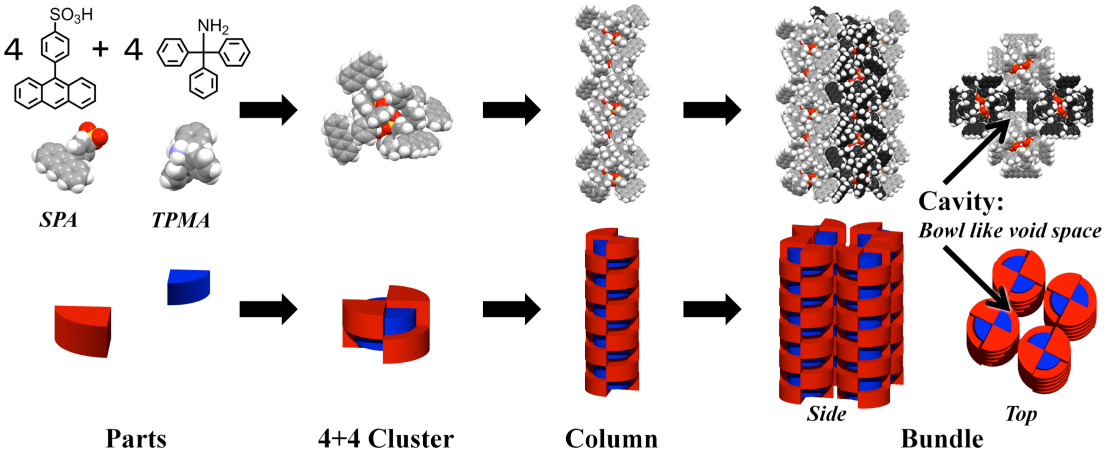

Fig. S1 Hierarchical construction and schematic depiction of a porous organic salt composed of 9(4-sulfophenyl)anthracene (SPA) and triphenylmethylamine (TPMA).

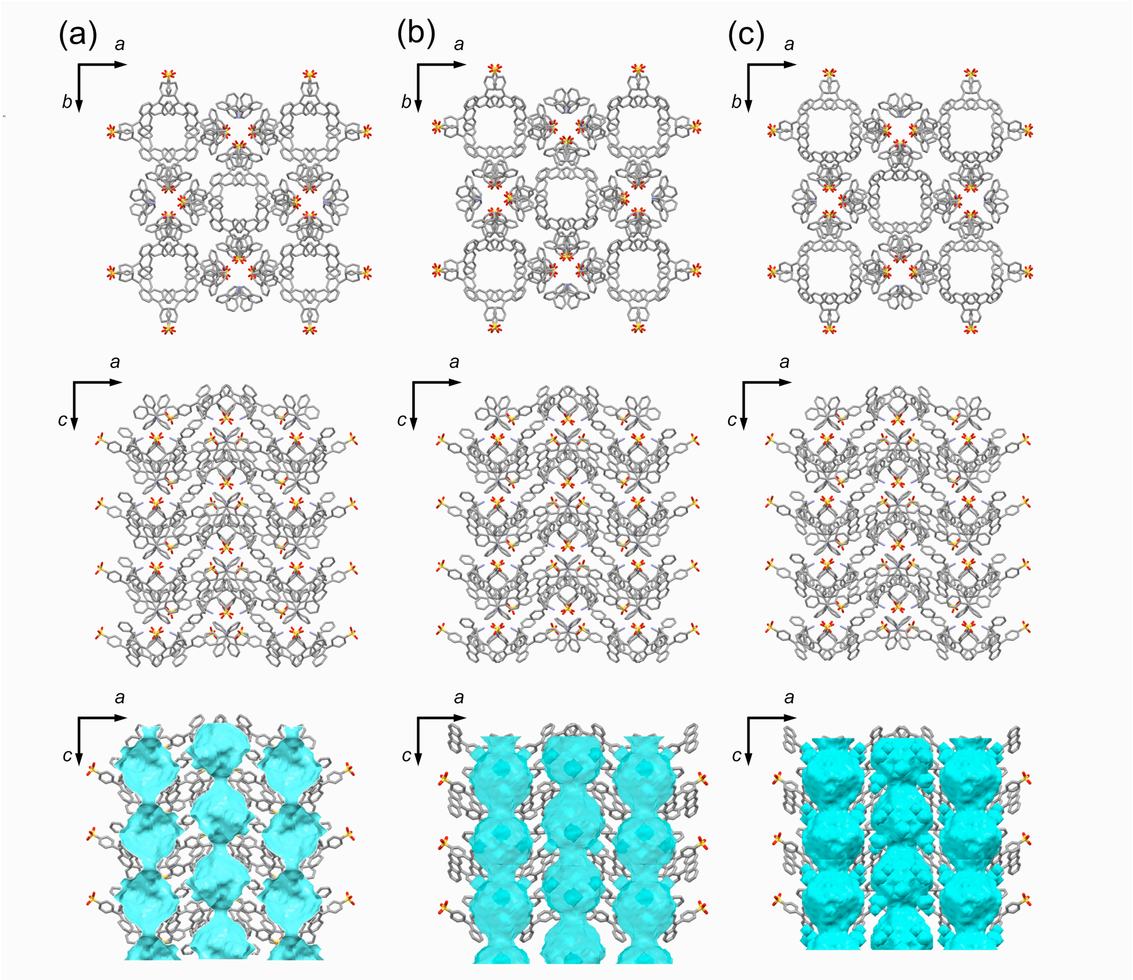

Fig. S2 Crystal structures of SPA/TPMA accommodating (a) *o*-dichlorobenzene, (b) C_{60}, and (c) C_{70}, respectively. Inclusions and hydrogen are omitted for clarity. View along the *b* axis in upper panels. View along the *c* axis in middle panels. Lower panels show visualization of void space of porous structures. Surface of void space is represented in sky blue.

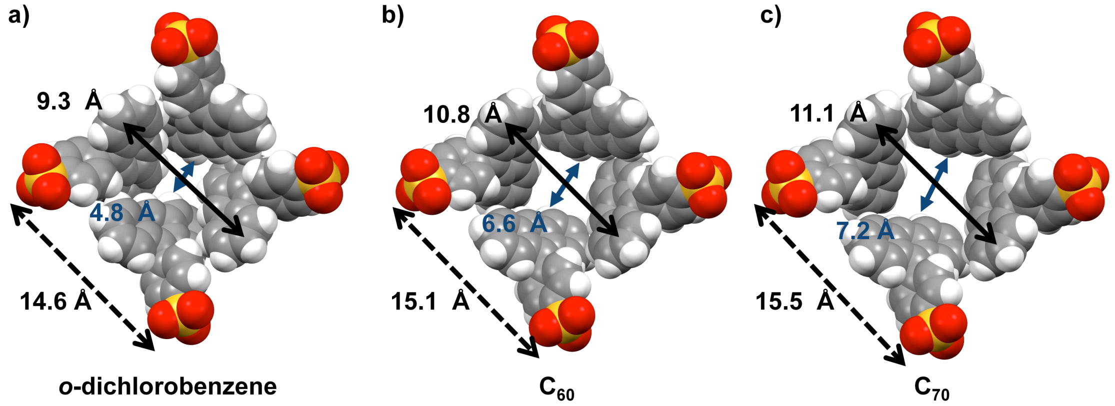

Fig. S3 Molecular arrangement of bowl like void spaces for (a) *o*-dichlorobenzene, (b) C_{60}, and (c) C_{70}, respectively. Solid double arrow, blue double arrow and dashed double arrow show diameter of bowl like void space, bottleneck size of porous structure and distance between columns.

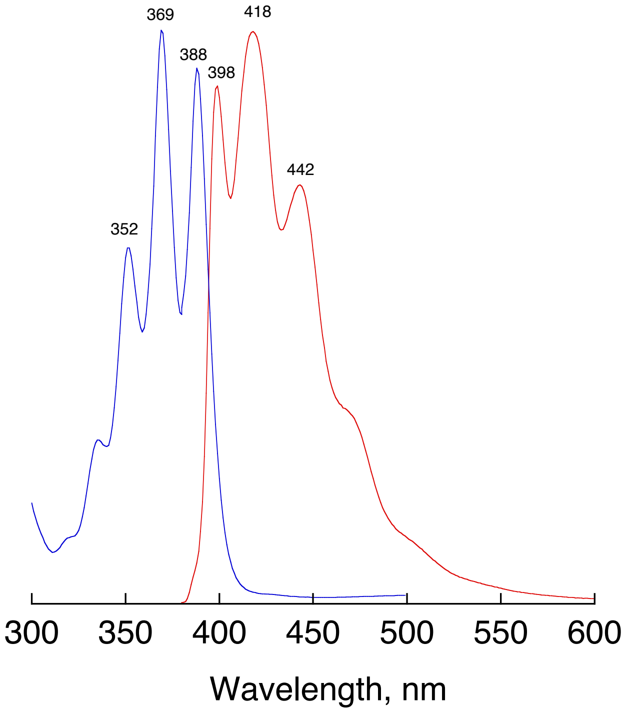

Fig. S4 UV-vis (blue) and fluorescence (red) spectra of SPA/TPMA in PhCN at 298 K.

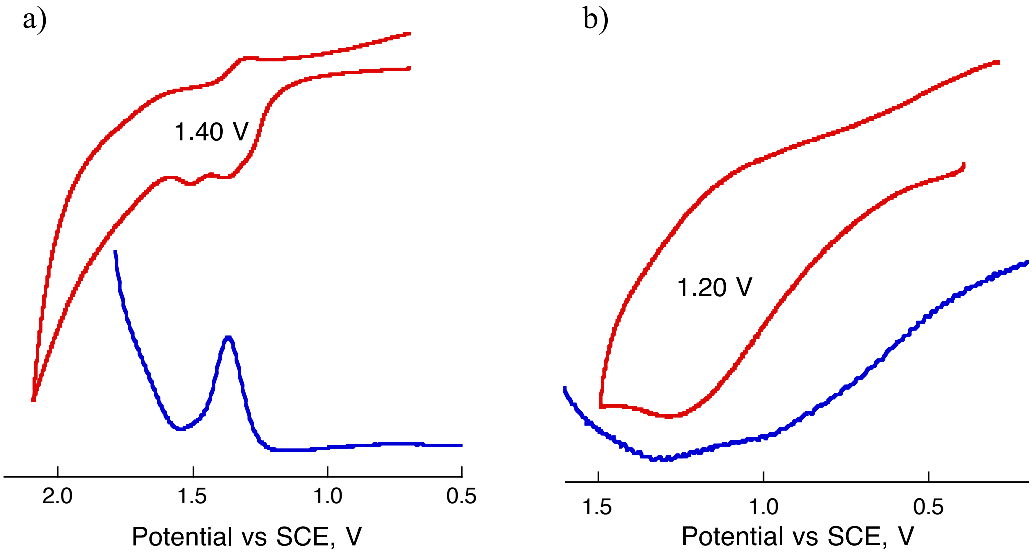

Fig. S5 CV (red) and DPV (blue) of (a) SPA/TPMA and (b) TFA/TPMA (5.0×10^{-4} M) recorded in PhCN containing $TBAPF_6$ (0.10 M). Scan rate: 100 mV s^{-1} for CV, 4 mV s^{-1} for DPV

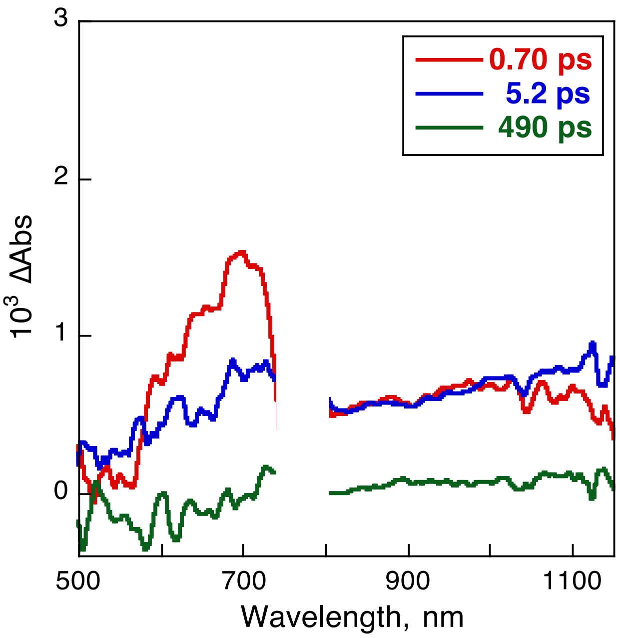

Fig. S6 Transient absorption spectra of a KBr pellet containing SPA/TPMA/C_{70} recorded at 0.7, 5.2, and 490 ps after femtosecond laser excitation at 393 nm.

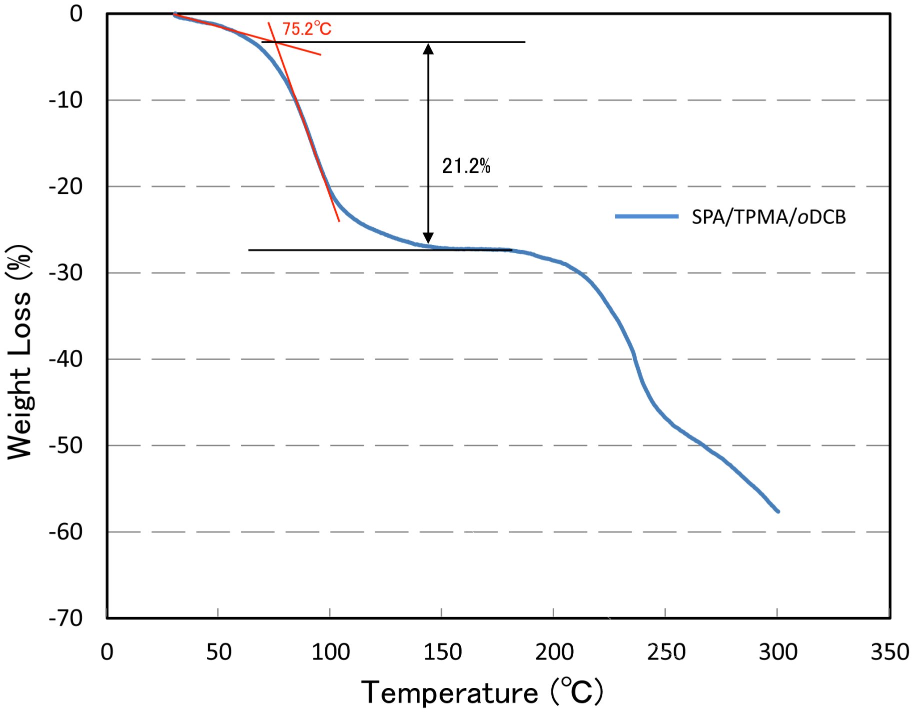

Fig. S7 Thermogravimetric analysis of the inclusion crystal: SPA/TPMA/*o*DCB. The first weight loss is 21.2%. The host guest ratio is *ca*. 1:1.1.