Electronic Supplementary Information for

An Organogel System can Control the Stereochemical Course of Anthracene Photodimerization

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General: All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals, Wako Organic Chemicals and used as received. The ^{1}H NMR spectra were recorded on a Bruker 300 (300 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. Mass spectral data were obtained using a Perspective Biosystems Voyager - DE RP MALDI-TOF mass spectrometer. Circular dichroism (CD) spectra were measured in JASCO J-720WI spectropolarimeter. UV spectra were recorded in a Shimadzu UV-2500 PC UV-VIS recording spectrophotometer. Luminescence spectral measurements were performed using a Perkin Elmer LS 55 luminescence spectrometer. IR spectra were obtained using a Perkin Elmer Spectrum One FT-IR spectrometer.

SEM measurements: A thin layer of gel sample was prepared over a carbon-coated copper grid and dried in vacuum for 24 hrs to obtain the xerogel. The sample was then shielded by Pt and examined with a Hitachi S-5000 scanning electron miscroscope.

XRD Studies: X-ray data were recorded on a Rigaku R-axis instrument. Gel sample was prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was evaporated in vacuum for 24 h. The obtained xerogel was put into a glass capillary (d = 0.7 mm). X-ray diffractogram was recorded on an imaging plate using Cu radiation (λ = 1.54178 Å).

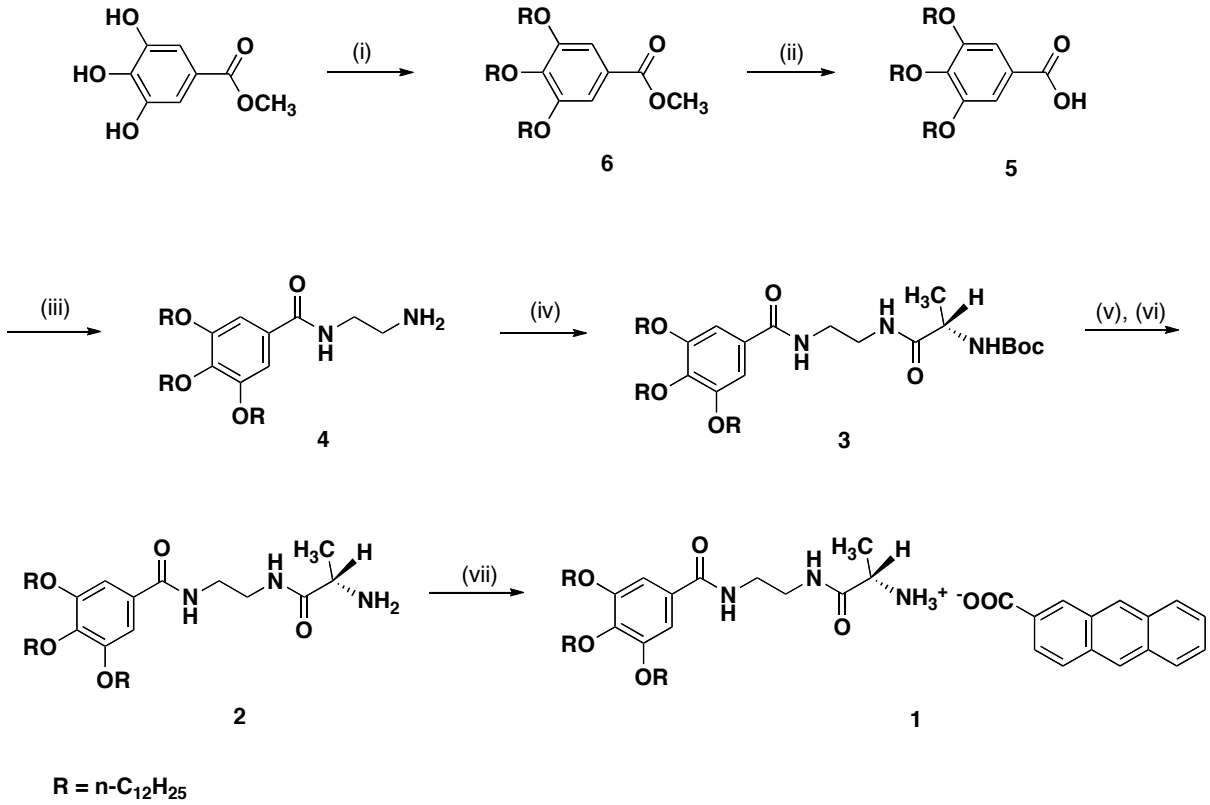
General procedure for photochemical reaction, product isolation and product analysis:

The cyclohexane gel of the binary gelator **1** was prepared in a capped quartz cell of 1 mm path length under argon atmosphere and irradiated at an wavelength 366 nm with a USHIO Optical Modulex Deep UV 500 through optical filters UV-35 and UV-D36C at constant temperature.

After the photo reaction, first the solvent (cyclohexane) was removed at 55 ^{0}C and finally in high vacuum for 24 h. The dried product was then dissolved in minimum amount of THF and poured in to a 25 mM borate buffer solution of pH 9 to precipitate the gelator backbone containing gallic ester coupled with alanine. The mixture was then filtered to collect the photoproducts and unreacted 2Ac as filtrate. 10 μl of this filtrate solution (50 mM) was subjected to the HPLC analysis. Same procedure was employed for the sol system. For the photoreaction in THF, the gelator backbone was isolated and precipitated directly by adding the reaction mixture (after photoreaction) to the borate buffer of pH 9. For solid-state reaction, the solid sample after photoreaction was dissolved in minimum volume of THF and then same procedure was employed as described above.

Analysis of the photoproducts was performed using chiral HPLC with tandem columns Inertsil ODS-2 (GL Sciences) and CHIRALCEL OJ-RH (Daicel).[1] The columns were kept at 35 ^{0}C. A mixture of 0.2 M potassium dihydrogen phosphate (adjusted to pH 2.5 by phosphoric acid) and acetonitrile (62:38 by volume) was used as an eluent. Relative yield and enantiomeric excess (ee) were determined by the peak area on the HPLC chromatogram detected by the absorbance at 254 nm.

Scheme S1 Synthesis of the binary gelator



Reagents and conditions: (i) 1-bromododecane, K_2CO_3, DMF, 60 ^{0}C, 20 h; (ii) NaOH, 1,4-dioxane/water, reflux, 20 h; (iii) ethylenediamine, BOP, CH_2Cl_2, RT, 3h; (iv) N-Boc-D-alanine, triethylamine (TEA), BOP, CH_2Cl_2, RT, 3h; (v) trifluoroacetic acid (TFA), CH_2Cl_2, RT; (vi) TEA, CH_2Cl_2, RT; (vii) 2-anthracenecarboxylic acid (2Ac), THF, RT, 2h.

Synthesis: Compound **2** was synthesized according to the scheme S1 and confirmed by ^{1}H NMR, MALDI-TOF mass measurements and elemental analysis. Compound **5** was synthesized by a method as described earlier. Methyl-3,4,5-trihydroxybenzoate was converted into its ether **6** by the reaction with 1-bromododecane. Subsequent hydrolysis of the ester group with NaOH yielded **5**.

Synthesis of 4: Compound **5** (3.0 g, 4.4 mM) was dissolved in dry CH_2Cl_2 (50 ml). BOP reagent (2.16 g, 4.9 mM) and ethylenediamine (1.34 g, 22.3 mM) were added to the solution and the reaction mixture was stirred for 3 h at RT under Ar atmosphere. The progress of the reaction was checked by TLC. The reaction mixture was first diluted with excess CH_2Cl_2 and then the organic layer was washed with brine three times. The collected organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was dried under reduced pressure. The solid was dissolved in minimum volume of $CHCl_3$ and re-precipitated in methanol. The mixture was kept at low temperature (0^0C) for 1 h and the residue was collected by filtration. The resultant residue was subjected to column chromatography [silica gel, $CHCl_3$/ MeOH = 20:1 (v/v)] to give compound **4** (2.8 g, 89%) as a white solid. ^{1}H NMR (300 MHz; $CDCl_3$; TMS): δ = 0.85-0.89 (9H, m), 1.26-1.31 (48H, m), 1.44-1.48 (6H, m), 1.71-1.73 (2H, m), 1.78-1.81 (4H, m), 2.95 (2H, t, J = 5.9), 3.48 (2H, q, J = 5.7), 3.99 (6H, m), 6.57 (1H, t, J = 5.4), 6.97 (2H, s); MS (MALDI-TOF, matrix; dithranol): m/z calcd for $[M + H]^+$; 717.65

found 717.82; Elemental analysis: calcd for $C_{45}H_{84}N_2O_4$; C 75.36, H 11.81, N 3.91, found C 75.13, H 11.77, N 3.90.

Synthesis of 3: Compound **4** (1 g, 1.4 mM), N-Boc-D-alanine (316 mg, 1.6 mM) and BOP reagent (680 mg, 1.5 mM) were dissolved in dry CH_2Cl_2 (25 ml). TEA (151 mg, 1.5 mM) was added and the reaction mixture was stirred for 4 h at RT under Ar atmosphere. The progress of the reaction was checked by TLC. The organic layer was washed three times with brine, dried over anhydrous Na_2SO_4, filtered and the filtrate was dried under reduced pressure. The dried solid was subjected to column chromatography [silica gel, $CHCl_3$/ MeOH = 20:1 (v/v)] to give compound **3** (1.1 g, 88%) as a white solid. ^{1}H NMR (300 MHz; $CDCl_3$; TMS): δ= 0.85-0.88 (9H, m), 1.26-1.31 (51H, m), 1.40 (9H, s), 1.44-1.48 (6H, m), 1.71-1.73 (2H, m), 1.78-1.81 (4H, m), 3.49 (2H, m), 3.57 (2H, m), 4.00 (6H, m), 4.11 (1H, q, *J* = 6.3), 4.92 (1H, m), 6.81 (1H, m), 7.01 (2H, s), 7.11 (1H, m); MS (MALDI-TOF, matrix; dithranol): m/z calcd for $[M + Na]^+$; 910.72 found 910.72; Elemental analysis: calcd for $C_{53}H_{97}N_3O_7$; C 71.66, H 11.01, N 4.73, found C 71.39, H 11.02, N 4.75.

Synthesis of 2: In the deprotection step,[2] compound **3** (1 g, 1.1 mM) was dissolved in dry CH_2Cl_2 (3 ml) and TFA (40 eq) was added slowly at RT. Stirring was continued until TLC showed the consumption of all starting material. Then the mixture was concentrated. Methanol was coevaporated several times to remove traces of TFA to give TFA salt of deprotected amino compound. The salt was neutralized by stirring with TEA (2 eq) in dry CH_2Cl_2 at RT with simultaneous checking of the completion of neutralization by TLC. The mixture was then washed three times with brine. Organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was dried under reduced pressure to give compound **2** (779 mg, 90%) as white solid. ^{1}H NMR (300 MHz; $CDCl_3$; TMS): δ = 0.85-0.88 (9H, m), 1.26-1.32 (51H, m), 1.45-1.48 (6H, m), 1.72-1.74 (2H, m), 1.78-1.80 (4H, m), 3.48 (2H, m), 3.55 (2H, m), 3.97 (6H, m), 4.03 (1H, q, *J* = 3.6), 7.03 (2H, S), 7.29 (1H, m), 7.83 (1H, m); MS (MALDI-TOF, matrix; dithranol): m/z calcd for $[M + Na]^+$; 810.67 found 810.77; Elemental analysis: calcd for $C_{48}H_{89}N_3O_5$; C 73.14, H 11.38, N 5.33, found C 72.97, H 11.41, N 5.31.

Preparation of 1: Equimolar quantities of compound **2** and 2Ac were stirred in THF at RT for 2h. The reaction mixture was concentrated under reduced pressure and finally dried in vacuum to give binary gelator **1** as yellow coloured solid. Elemental analysis: calcd for $C_{63}H_{99}N_3O_7$; C 74.88, H 9.88, N 4.16, found C 74.85, H 9.91, N 4.14.

Preparation of gel: Gelator and the solvent were taken in a capped glass tube and the mixture was heated until the solid was dissolved. The sample was then quenched in air to 25 ^{0}C and left for 1 h at this temperature. The gelation state of the material was evaluated by 'stable-to-inversion of a test tube' method.

Gel-sol transition temperature (T_{gel}): T_{gel} was measured by the test-tube-tilting method where a test tube containing the gel was immersed inversely in a thermostatted bath and the temperature was raised at 0.5 ^{0}C/min. The T_{gel} was considered as the temperature when the mass was started to flow.

References

1. (a) A. Nakamura, and Y. Inoue, *J. Am. Chem. Soc.*, 2005, **127**, 5338; (b) A. Nakamura, and Y. Inoue, *J. Am. Chem. Soc.*, 2003, **125**, 966.
2. S. C. Ceide, L. Trembleau, G. Haberhauer, L. Somogyi, X. Lu, T. Bartfai and J. Rebeck, Jr., *Proc. Natl. Acad, Sci. USA*, 2004, **101**, 16727.

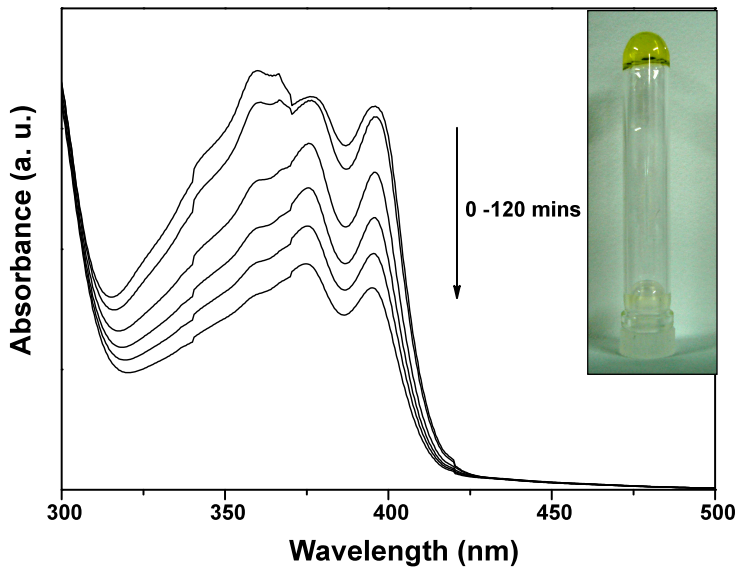


Fig. S1 UV-Vis spectra of the gel sample of **1** (9.9 x 10^{-3} mol dm^{-3}) in cyclohexane with progress of photoirradiation at 10 °C (Inset: photograph of gel **1**).

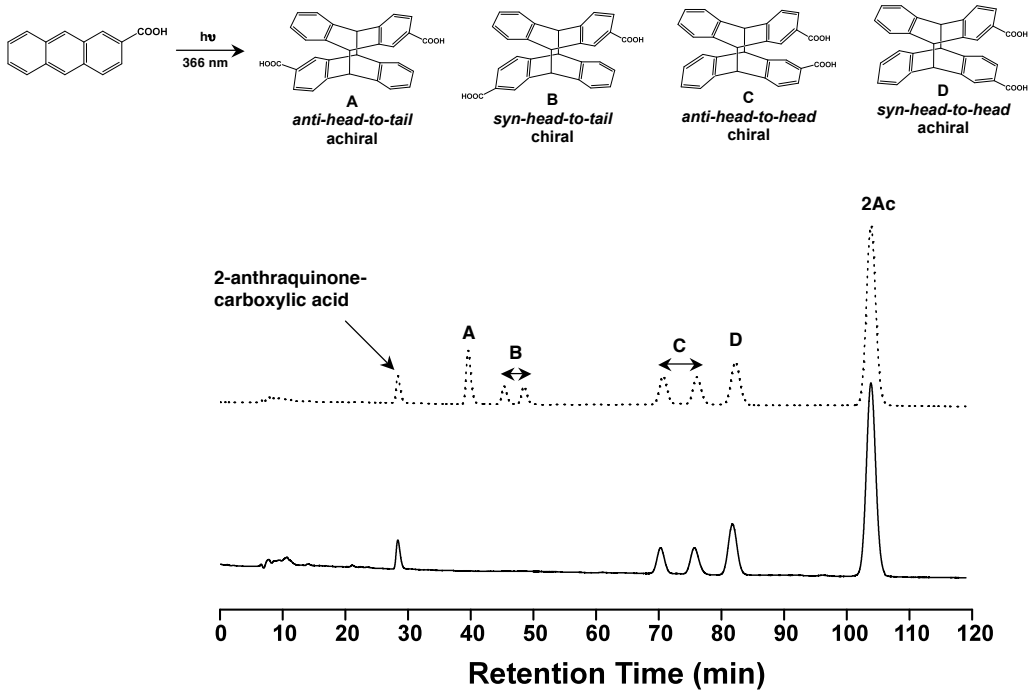


Fig. S2 Typical HPLC chromatograms of the photoirradiated samples obtained from cyclohexane gel of **1**(solid line) and reference sample (dotted line) to assign peaks.

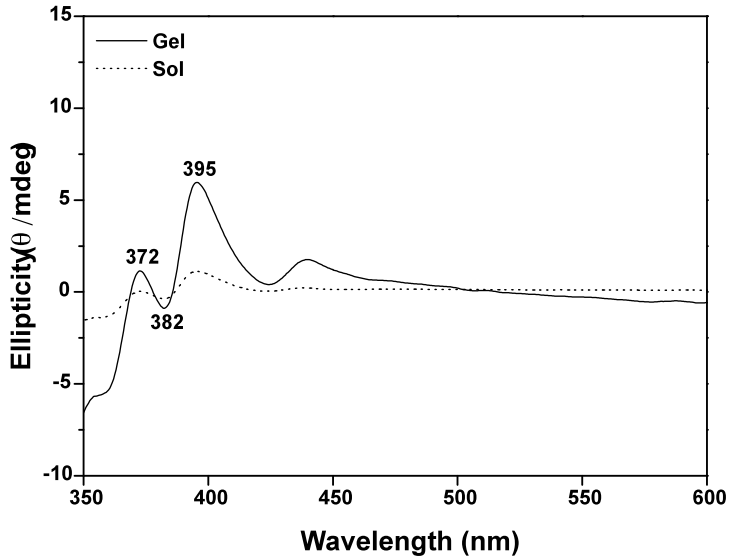


Fig. S3 Circular dichroism spectra of the sample **1** in the gel (25 °C) state and in the sol (50 °C) state prepared from cyclohexane (9.9 x 10^{-3} mol dm^{-3}).

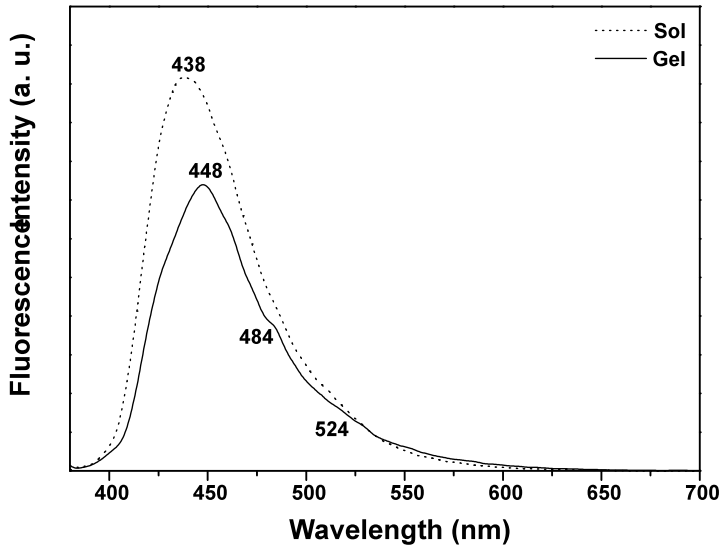


Fig. S4 Fluorescence spectra of the sample **1** in the gel (25 °C) state and in the sol (50 °C) state prepared from cyclohexane (9.9 x 10^{-3} mol dm^{-3}).

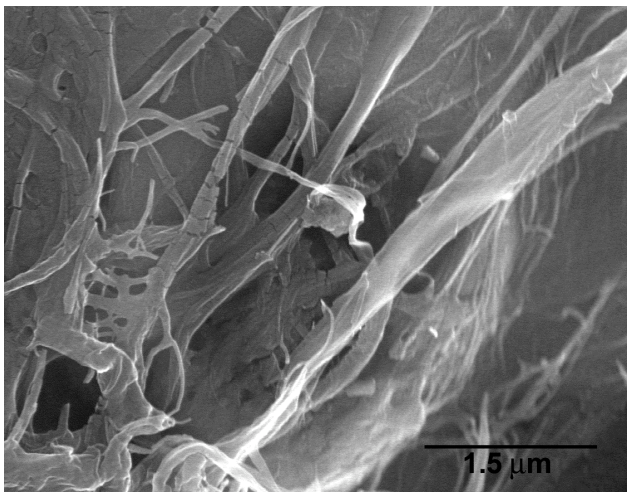


Fig. S5 SEM image of xerogel of **1** (9.9 x 10^{-3} mol dm^{-3}) prepared in cyclohexane.

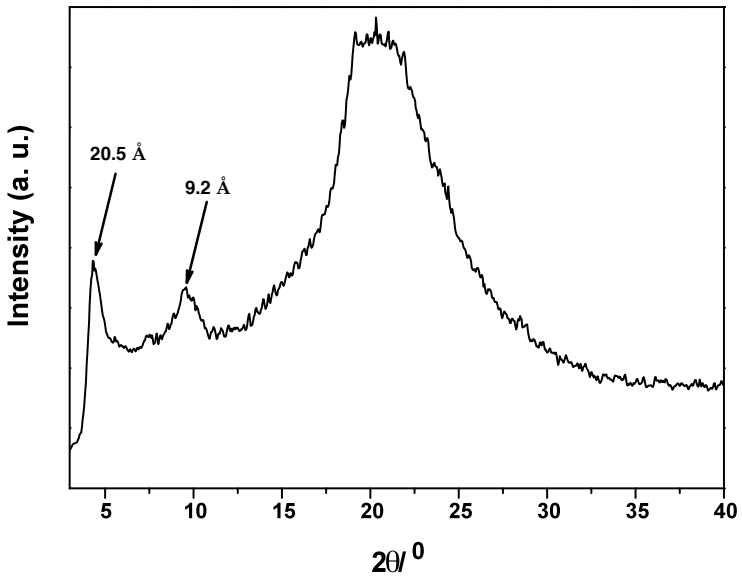


Fig. S6 X-ray diffractogram of the xerogel of sample **1** prepared from cyclohexane (9.9 x10^{-3} mol dm^{-3}).

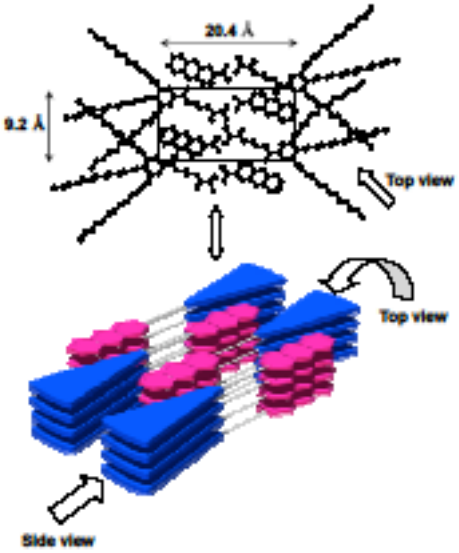


Fig. S7 Molecular scales and proposed packing model of **1** in the cyclohexane gel.

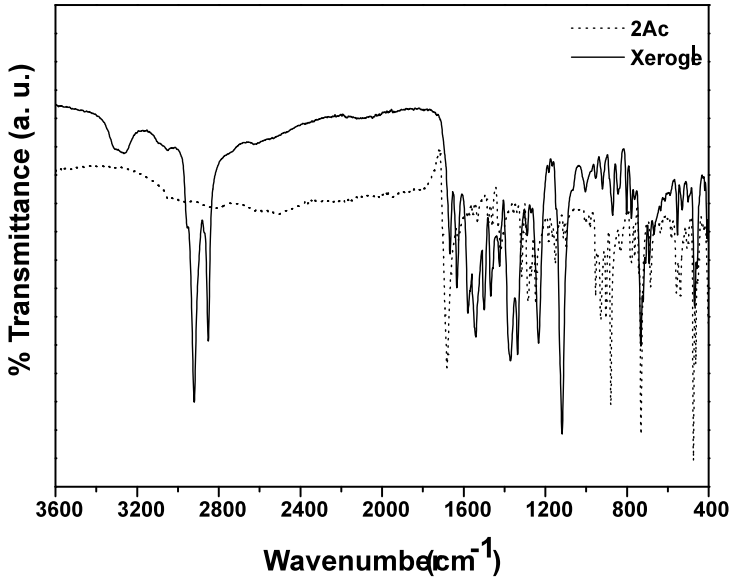


Fig. S8 FT-IR spectra of 2Ac and xerogel of sample **1** (9.9×10^{-3} mol dm^{-3}) prepared in cyclohexane.