

Supporting Information

Three-arm star compounds composed of 1, 3, 5-tri(azobenzeneethynyl)benzene cores and flexible PEO arms: Synthesis, optical functions, hybrid Ormosil gel glasses

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General. Methanol (AR), phenol (AR), 4-bromoaniline (AR), sodium nitrite(AR), potassium hydroxide (AR) and toluene-*p*-sulfonyl chloride (AR) were purchased from Beijing chemical factory and used without further purification. Poly(ethylene oxide) (*M*_w = 550, Acros) was refluxed with benzene and disposed of residue water in PEO by a oil-water separator. Pyridine(AR, Beijing chemical factory) was refluxed with calcium hydride and distilled just before use. Tetrahydrofuran (THF, AR, Beijing chemical factory) was refluxed over calcium hydride and then refluxed over sodium together with benzophenone and distilled when the refluxing mixture turned blue. 1, 3, 5-triiodobenzene was synthesized according to literature [1-2].

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker ARX-300 Nuclear Magnetic Resonance spectrometer (CDCl₃ or DMSO-D₆ as solvent, TMS as inner standard). MALDI-TOF mass spectra were measured on a Bruker Biflex III spectrometer with CCA (α-cyano-4-hydroxycinnamic acid) as matrix. Elemental analysis of C, H, and N was completed through the Heratus CHN-Rapid method. The glass transition temperatures (T_g) of the compounds were tested with a TA Instruments DSC 2910 at a heating rate of 10 °C/min under N₂ protection. UV-vis spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer. SAXS diagrams were performed on a Panalytical SAXSess System (Holand). The range of scattering angle was chosen from s

Z 0.05 to 6 nm⁻¹ (scattering vectors = $2\pi\sin\theta/\lambda$, where 2θ and λ were the scattering angle and an X-ray wavelength of 0.154 nm, respectively). Scanning Electron Spectroscopy (SEM) determination was carried out with Hitachi S-4300 field emission scanning electron microscope. Gold powder was sprayed over the fresh sample surface for clearness of image. UV-VIS-near IR transmittance spectra were measured on Varian Cary 5000 UV-visible-near infrared absorption spectrophotometer. To obtain IR spectra, each sample was ground with KBr powder and the transmittance of each resulting pellet was measured with an FTIR spectrophotometer (Varian Excalibur 3100).

The optical limiting properties were investigated using 8 ns laser pulses from a Nd:YAG laser (Spectra-Physics Quanta-Ray INDI Pulsed Nd:YAG Laser, optical parametric oscillator) at a repetition rate of 10 Hz, and at wavelengths of 532 nm. The pulse energies in front of and behind the sample were monitored by energy detectors D1 and D2 (Ophir Optronics Inc. PE25). The laser beam waist was approximately 7.0 μm (532 nm). All measurements were conducted at room temperature. The solution was contained in 5 mm thick quartz cells, while the solid glass was fixed vertically using a clamp. The third order nonlinear optical properties of the compound **1** in ethanol solution and its gel glass were studied using Z-scan technique with Nd-YAG laser as light source (the pulse width of 5 ns and wavelength of 532 nm).

1. Synthetic procedure.

4-(4-Bromo-phenylazo)-phenol (**4**): A solution of NaNO₂ (20.07 g, 0.3 mol in 104 mL H₂O) was dropped into a mixture of 4-bromoaniline (30.96 g, 0.18 mol), hydrochloric acid (36%, 60 mL) and H₂O (120 mL) while stirring at 0~5 °C for 30 min. After a pistachio solution of the diazonium salt was formed, it was added dropwise into a solution of phenol (16.94 g, 0.18 mol), NaOH (7.2 g, 0.18 mol) and Na₂CO₃ (16.96 g, 0.16 mol) in H₂O (120 mL) at 0~5 °C. The mixed system was agitated for 60 min and its pH was adjust to 2~3. The product was collected by filtration, washed with water until the pH of the filtrate was about 7 and dried. The crude product was purified by dissolving in ethanol and precipitating by water twice and dried under vacuum oven for 48 h. Yield: 73.2%. Mp. 152-154 °C. ¹H NMR (DMSO-d₆, ppm): δ 10.40 (s, O-H, 1H), 7.82 (d, Ar-H, 2H), 7.80 (t, Ar-H, 4H), 6.95 (d, Ar-H, 2H).

4-((4-(3-Hydroxy-3-methylbut-1-ynyl)phenyl)diazonyl)phenol (**5**): A 250 mL flask

were charged with 4-(4-bromo-phenylazo)-phenol (**4**) (1.385 g, 5 mmol), bis(triphenylphosphine)palladium(II) chloride (0.035 g, 0.05 mmol), CuI (0.048 g, 0.25 mmol), triphenylphosphine (0.131 g, 0.5 mmol). Subsequently, 100 mL of triethylamine, and 0.63 g (46.4 mmol) of 2-methyl-3-butyne-2-ol were added to the flask successively. The resulting mixture was heated to 70 °C under nitrogen for 24 h before the solvent was removed under vacuum. The residue was extracted with ethyl acetate and washed three times with saturated aqueous NH₄Cl. The organic layer was dried over MgSO₄ and then concentrated in vacuum to give a crude solid. The residue was purified by column chromatography (2:1, petroleum ether: ethyl acetate) to afford a tan solid of **5** (1.34g, 95.7%). Mp. 190-192 °C. ¹H NMR (DMSO-d₆, ppm): δ 10.35 (s, ArO-H, 1H), 7.81 (d, Ar-H, 4H), 7.67 (t, Ar-H, 2H), 6.95 (d, Ar-H, 2H), 1.49 (t, CH₃-H, 6H).

4-(4-Ethynyl-phenyl diazonyl)phenol (**6**): Potassium hydroxide (0.6 g, 10 mmol) and 4-((4-(3-hydroxy-3-methylbut-1-ynyl)phenyl)diazonyl)phenol (**5**) (1.26 g, 4.5 mmol) were dissolved in 1,4-dioxane (200 mL) in a round-bottom flask equipped with a Dean-Stark trap fitted with a reflux condenser. The mixture was heated at 120 °C for 6 h, cooled to room temperature, added 6 mol/L hydrochloric acid, extracted with ethyl acetate, washed with water, dried (MgSO₄), filtered, and concentrated. The resulting solution was passed through a short silica gel column eluting with petroleum ether/ethyl acetate (1/3) to give **6** as a tan powder in 60% yield. Mp. 154-157 °C. ¹H NMR (CDCl₃, ppm): δ 10.35 (s, ArO-H, 1H), 7.87 (m, Ar-H, 4H), 7.62 (t, Ar-H, 2H), 6.96 (d, Ar-H, 2H), 3.21 (s, C-H, 6H).

Methoxy poly (ethylene oxide) ethoxy tosylate (PEO-Ts): Poly(ethylene oxide) monomethyl ether ($\{M_w\} = 550$, 11.0 g, 20 mmol) was dissolved in 20 mL dry pyridine under nitrogen. A solution of toluene-p-sulfonyl chloride (4.58 g, 24 mmol) in 20 mL dry pyridine was then added dropwise to the above mixture. The reaction mixture was stirred overnight under nitrogen. The resulting solution was poured into water and extracted with methylene chloride. The organic layer was washed with diluted hydrochloric acid and water three times, respectively, dried over anhydrous MgSO₄, and concentrated in vacuo. The product was purified by column chromatography (THF as eluent) to yield 11.4 g (80%) of a colorless oil. ¹H NMR (CDCl₃, ppm): δ 7.80 (d, Ar-H, 4H), 7.35 (d, Ar-H,

2H), 4.16 (t, PEO-*H*, 2H), 3.67-3.58 (m, PEO-*H*), 3.38 (s, PEO-*H*, 3H), 2.34 (s, Ar-CH₃-*H*, 3H).

4-((4-Ethynylphenyl)diazonyl)phenol poly(ethylene oxide) ether (**7**). 1.11 g (5 mmol) 4-((4-ethynylphenyl)diazonyl)phenol (**6**), 0.56g (10 mmol)potassium hydroxide and 80 mL methanol were added to a 250 mL three-neck flask under argon atmosphere, the mixture was refluxed for two hour. A solution of 3.52 g (5 mmol) PEO-Ts in 20 mL methanol was added to the flask. The reaction mixture was refluxed for 48 hours. After cooling, the reaction mixture was poured into 100 mL water, adjust PH of the solution to slightly acidity by using hydrochloric acid. Extracted with methylene chloride, the methylene chloride solution was washed with water three times, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the product was purified by column chromatography (silica gel, THF as eluent) to yield a tan oil. Yield: 49.2%. ¹H NMR (CDCl₃, ppm): δ 7.87 (m, Ar-*H*, 4H), 7.62 (t, Ar-*H*, 2H), 6.96 (d, Ar-*H*, 2H), 4.19 (t, PEO-*H*, 2H), 3.83 (t, PEO-*H*, 2H), 3.75- 3.56 (m, PEO-*H*), 3.36 (s, PEO-*H*, 3H), 2.42 (s, C-*H*, 1H).

Three-arm Star-shaped compound (**1**): A heavy-walled Schlenk flask was charged with 1, 3, 5-triiodobenzene (0.146 g, 0.32 mmol), copper(I) iodide (0.18 equiv, 0.011g), bis(triphenylphosphine)palladium(II) chloride (0.05 equiv, 0.011 g) and triphenylphosphine (0.5 equiv, 0.037 g). The flask was degassed and back-filled with nitrogen three times. Next, degassed triethylamine (20 mL) and compound **7** (0.964 g, 1.28 mmol) were added. After stirring the mixture at 60 °C for 65 h, saturated aqueous NH₄Cl (300 mL) was added, and the resulting mixture was extracted with ethyl acetate. The solvent was evaporated, and the crude mixture was purified by column chromatography (20:1 CH₂Cl₂:methanol) two times to afford **1** as a dark red half-solid (0.77 g, 74.1%). ¹H NMR (CDCl₃, ppm): δ 7.92 (q, Ar-*H*, 12H), 7.72 (s, Ar-*H*, 3H), 7.67 (s, Ar-*H*, 6H), 7.04 (d, Ar-*H*, 6H), 4.22 (t, PEO-*H*, 6H), 3.89 (t, PEO-*H*, 6H), 3.73- 3.54 (m, PEO-*H*), 3.38 (s, PEO-*H*, 9H). MS (MALDI-TOF): m/z (M⁺) =2255.6, 2299.6, 2343.8, 2387.6, 2431.8, 2475.8, 2519.7, 2563.7, 2607.8, 2651.8, 2695.9, 2740.0, 2753.9.

In the 300MHz ¹H NMR spectrum of **1** (Figure S1), resonant peaks of δ = 3.38 ppm correspond to methyl proton **a** and δ =3.55~3.76, 3.90 and 4.20 ppm correspond to methylene proton **b**, **c** and **d**. Resonance absorbing peaks of aryl proton are in the area of

$\delta = 7.02\sim 7.94$ ppm. From the aggregation area ratio of methylene proton and methyl proton, we can calculate the repeating number of PEO is 3×13 . From the aggregation area ratio of alkyl proton and aryl proton, we can calculate the number of benzene is seven. So the M_n of **1** is 2496.35, which fits well with the calculated value.

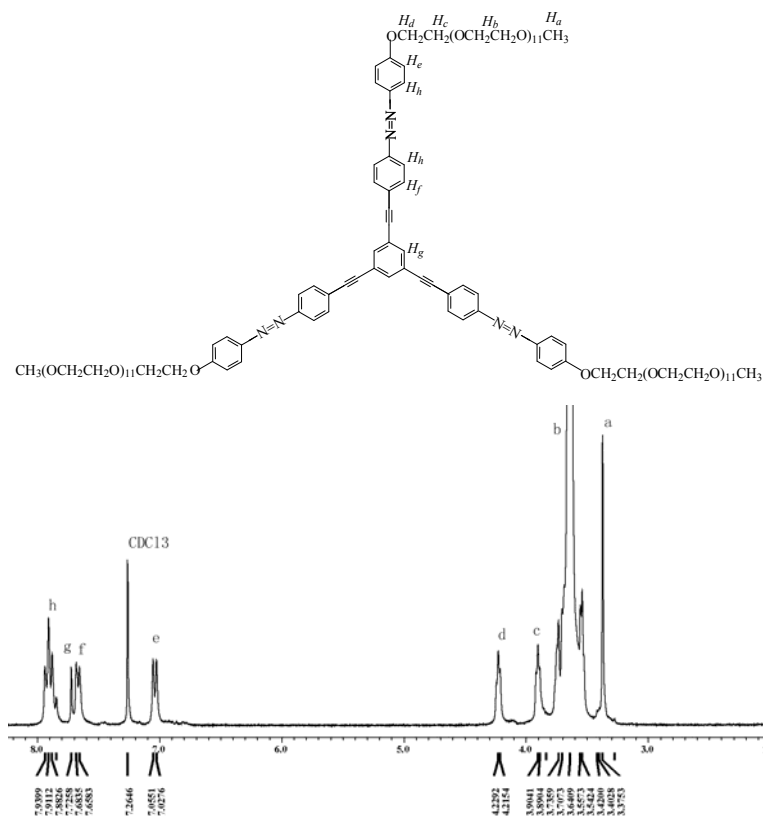


Figure S1. ^1H NMR spectrum of star-shaped block compound **1**

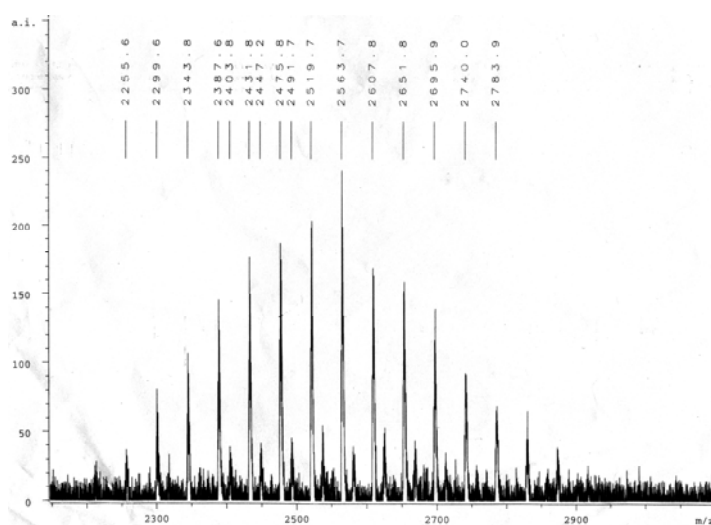


Figure S2. MALDI-TOF spectrum of compound **1**

Figure S2 is the complete MALDI-TOF mass spectrum of compound **1**. There are two series of equidistant mass peaks, indicating that different molecular ions were formed. The main series of mass peaks are assigned to the sodium ion adducts of compound **1**; the second series is correspondent to the mass of potassium ion adducts of molecules. The molecular weight difference of two adjacent peaks in each series is 44, which corresponds to the molecular weight of the repeating unit of PEO. From the characterization results MALDI-TOF mass spectrum and 300MHz ^1H NMR spectrum, we can conclude that we obtain the designed targeting molecule.

4,4',4''-(4,4',4''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(benzene-4,1-diyl))tris(diazene-2,1-diyl)triphenol (**3**): A heavy-walled Schlenk flask was charged with **1**, 3, 5-triiodobenzene (0.228 g, 0.5 mmol), bis(triphenylphosphine) palladium(II) chloride (0.02 mmol, 0.014 g), copper(I) iodide (0.1 mmol, 0.019 g), and triphenylphosphine (0.2 mmol, 0.0526 g). The flask was degassed and back-filled with nitrogen three times. Next, degassed triethylamine (20 mL) and 4-(4-ethynyl-phenyl diazonyl)phenol (**5**) (0.444 g, 2 mmol) were added. After stirring the mixture at 60 °C for 48 h, saturated aqueous NH_4Cl (300 mL) was added, and the resulting mixture was extracted with ethyl acetate. The solvent was evaporated, and the crude mixture was purified by column chromatography (6:1 CH_2Cl_2 : ethyl acetate) two times to afford **3** as a dark red half-solid (0.288 g, 77.9%). Mp. 241-243 °C. ^1H NMR (CDCl_3 , ppm): δ 10.46 (s, ArO-*H*, 3H), 7.88-7.93 (m, Ar-*H*, 18H), 7.01 (d, Ar-*H*, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 161.33, 151.69, 145.23, 134.05, 132.65, 125.06, 123.43, 122.44, 115.96, 99.36, 90.66, 89.37. MS (MALDI) m/z : 739.1. Anal. Calcd for $\text{C}_{48}\text{H}_{30}\text{N}_6\text{O}_3$: C, 78.03; H, 4.09; N, 11.38. Found: C, 78.22; H, 4.15; N, 11.33.

1-(4-(Hexadecyloxy)phenyl)-2-(4-bromophenyl)diazene (**8**): Bromohexadecanol (6.10 g, 20 mmol), 4-(4-bromo-phenylazo)-phenol (**4**) (2.770 g, 10 mmol), K_2CO_3 (1.38 g, 10 mmol), and KI (1.66 g, 1 mmol) were dissolved in acetonitrile (30 mL). The mixture was stirred at 100 °C for 24 h. The resulting solution was cooled to room temperature and extracted with ethyl acetate. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed by evaporation. The product was purified by column chromatography (silica gel, CH_2Cl_2 /petroleum ether (1:2) as eluent) to yield 4.42 g (80.5%) of croci powder. ^1H NMR (CDCl_3 , ppm): δ 7.82 (d, Ar-*H*, 2H), 7.79 (t, Ar-*H*,

4H), 6.99 (d, Ar-*H*, 2H), 4.04 (t, OCH₂-*H*, 2H), 1.82 (m, OCH₂CH₂-*H*, 2H), 1.26 -1.44(m, CH₂-*H*, 26H), 0.88 (t, CH₃-*H*, 3H) .

1-(4-Ethynylphenyl)-2-(4-(hexadecyloxy)phenyl)diazene (**9**): A 250 mL flask was charged with **8** (2.745 g, 5 mmol), bis(triphenylphosphine) palladium(II) chloride (0.035 g, 0.05 mmol), CuI (0.048 g, 0.25 mmol), triphenylphosphine (0.131 g, 0.5 mmol). Then 100 mL of triethylamine and 0.63 g of 2-methyl-3-butyn-2-ol (46.4 mmol) were added to the flask successively. The resulting mixture was heated to 70 °C under nitrogen for 24 h before the solvent was removed under vacuum. The residue was extracted with ethyl acetate and washed three times with saturated aqueous NH₄Cl. The organic layer was dried over MgSO₄ and then concentrated in vacuo to give a crude solid. The residue was purified by column chromatography (2:1, petroleum ether: CH₂Cl₂) to afford a croci solid of 4-(4-((4-(hexadecyloxy)phenyl)diazenyl)phenyl)-2-methylbut -3-yn-2-ol.

This product (2.273 g, 4.5 mmol) and potassium hydroxide (0.660 g, 10 mmol) was dissolved in 1,4-dioxane (200 mL) in a round-bottom flask equipped with a Dean-Stark trap fitted with a reflux condenser. The mixture was heated at 120 °C for 9 h, cooled to room temperature, added 6 mol/L hydrochloric acid, extracted with ethyl acetate, washed with water, dried (MgSO₄), filtered, and concentrated. The resulting solution was passed through a short silica gel column eluting with petroleum ether/ethyl acetate (1/3) to give **9** as a croci powder in 65% yield. ¹H NMR (CDCl₃, ppm): δ 7.91 (d, Ar-*H*, 2H), 7.83 (d, Ar-*H*, 2H), 7.61 (d, Ar-*H*, 2H), 7.00 (d, Ar-*H*, 2H), 4.04 (t, OCH₂-*H*, 2H), 3.20(s, C-*H*, 1H), 1.82 (m, OCH₂CH₂-*H*, 2H), 1.26 -1.46(m, CH₂-*H*, 26H), 0.88 (t, CH₃-*H*, 3H).

1, 3, 5-Tris((4-((4-(hexadecyloxy)phenyl)diazenyl)phenyl)ethynyl)benzene (**2**): A heavy-walled Schlenk flask was charged with 1, 3, 5-triiodobenzene (0.228 g, 0.5 mmol), bis(triphenylphosphine) palladium(II) chloride (0.02 mmol, 0.014 g), copper(I) iodide (0.1 mmol, 0.019 g), and triphenylphosphine (0.2 mmol, 0.0526 g). The flask was degassed and back-filled with nitrogen three times. Next, degassed triethylamine (20 mL) and 1-(4-ethynylphenyl)-2-(4-(hexadecyloxy) phenyl)diazene (**9**) (0.444 g, 2 mmol) were added. After stirring the mixture at 60 °C for 48 h, saturated aqueous NH₄Cl (300 mL) was added, and the resulting mixture was extracted with ethyl acetate. The solvent was evaporated, and the crude mixture was purified by column chromatography (3:1 CH₂Cl₂: petroleum ether) to afford **2** as a dark red half-solid. Yield: 68.1%, Mp. 125 °C (by DSC).

^1H NMR (CDCl_3 , ppm): δ 7.92 (t, Ar-*H*, 12H), 7.72 (d, Ar-*H*, 3H), 7.68 (d, Ar-*H*, 6H), 7.00 (d, Ar-*H*, 6H), 4.05 (t, OCH_2 -*H*, 6H), 1.85 (m, OCH_2CH_2 -*H*, 6H), 1.26-1.48(m, CH_2 -*H*, 78H), 0.88 (t, CH_3 -*H*, 9H). MS (ESI) m/z : 1411.9. Anal. Calcd for $\text{C}_{96}\text{H}_{126}\text{N}_6\text{O}_3$: C, 81.66; H, 8.99; N, 5.95. Found: C, 81.48; H, 9.17; N, 5.85.

Preparation of hybrid Ormosil Gel Glasses: The materials were prepared by the hydrolysis and polycondensation of MTES in acidic medium (H_2O , acetic acid or HCl, pH=2.5) using a modified method reported in the literature.³⁻⁴ The molar ratio of MTES: ethanol: distilled water in the precursor was 3:1:3. The mixture was stirred overnight and evaporated to the initial volume of the MTES precursor. The mixture was stirring for 5-7 days. The ethanol or THF solution of compound **1-3** was added to the sol. After aging was finished, the gels were divided into several volume parts, cast into polypropylene cells individually, and dried 1-2 days at room temperature to give the final monoliths.

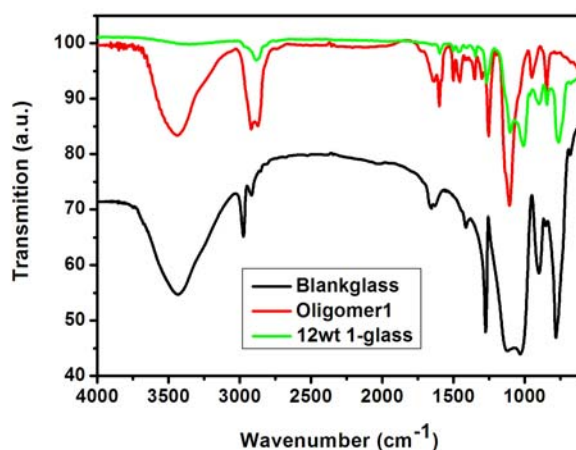


Figure S3. FT-IR spectra of compound **1**, blank MTES glass and **1**-MTES gel glass.

2. FT-IR spectra. The FT-IR spectra of pristine compound **1**, blank MTES glass and **1**-MTES gel glass are shown in Figure S3. In the spectrum of the **1**-MTES gel glass, the peaks of the OH stretching vibration of the residual silanol groups of blank gel glass (3435.2cm^{-1}) and compound **1** (3456cm^{-1}) are not present, instead of a peak of the OH stretching vibration of the residual silanol groups was observed at around 3338cm^{-1} . Peaks from the C-O-C stretching vibration of the $-\text{CH}_2\text{-O-CH}_2-$ in **1** and its gel glass

appeared at 1107.1 cm^{-1} and 1103.1 cm^{-1} , respectively. The vibration Si-O-Si double peak (1030 and 1122.5 cm^{-1} for blank MTES gel glass; 1010.5 and 1103.1 cm^{-1} for **1**-MTES gel glass) and Si-OH peak (906.5 cm^{-1} for blank; 895.0 cm^{-1} for **1**-MTES gel glass) are shifted to the lower wave number. All the relatively lower and weaker peaks of **1** was due to hybridization, and this confirmed the hydrogen bonding between the residual silanol groups in the MTES matrix and the $-\text{CH}_2\text{-O-CH}_2-$ groups of compound **1**.⁵⁻⁸

3. Photoisomerization Study. The *trans*-to-*cis* photoisomerization of the azo chromophores was induced by irradiating UV light, which was from a high-intensity 365 nm UV lamp equipped with 12.7 cm diameter filter (Cole-Parmer L-97600-05 long wave UV lamp, U-09819-23 filter). The intensity of the lamp was 7000 mW/cm^2 at a distance of 38 cm and 21000 mW/cm^2 at a distance of 5 cm. The samples were placed at ca. 15 cm away from the lamp. The surrounding temperature of the samples was controlled to be about $30\text{ }^\circ\text{C}$ by a cold plate. The UV-Vis spectra of the samples were measured over different irradiation time intervals by using an Agilent 8453 UV-Vis spectrophotometer. For the *trans*-to-*cis* isomerization study, the compounds dissolved in anhydrous DMF were irradiated with 365 nm UV light for different time intervals and the UV-vis spectra of the samples were recorded until the photostationary states were reached. For measuring the thermal *cis*-to-*trans* isomerization, the samples were kept in a dark oven with constant temperature ($30 \pm 1\text{ }^\circ\text{C}$), and the UV-Vis spectra were recorded over different time intervals.

From Fig. 1 in the article, the absorbance at λ_{max} before the light irradiation (A_{origin}) and the absorbance at the same wavelength after the irradiation for different time periods (A_t) can be obtained. The relative absorbance (A_t/A_{origin}) of the samples can be used to

indicate the relative amount of the trans isomers remaining at t time. The variations of A_t/A_{origin} with t represent the kinetics of the photoisomerization. The variations can be best fitted by the first-order exponential decay function,

$$A(t) = A_0 + A_1 \exp(-t/T_1) \quad (1)$$

where T_1 is the characteristic time of the decay process. Both data and fitting curve are shown in the insert of Fig. 1 in the article and the parameters obtained from the best fit are given in Table S1.

The isomerization degree of azo compounds (η) can be calculated by

$$\text{Isomerization Degree} = 1 - (A_s / A_{origin}) \quad (2)$$

where A_s is the 383 nm absorbance measured at the photostationary state. The result was given in Table S1.

Table S1. Parameters of the photoisomerization kinetics obtained from the curve fitting for the solutions (**1** and **2**, 0.023 g/L) and the corresponding photoisomerization degrees. Here: χ^2 is correlative coefficient; η is photoisomerization degree

Compound	A_0	A_1	T_1 (s)	χ^2	η
1	0.48775	0.50969	4.01881	0.9971	54.7%
2	0.24916	0.72934	5.13402	0.98984	76.4%

4. Third Order Molecular Hyperpolarizability

Table S2. The effective imaginary third order molecular hyperpolarizability ($\text{Im}\{\chi^{(3)}\}$) data for compound **1** in solution and gel glass.

Compound 1	2wt % Solution	2wt % Glass	12 wt % Glass
$(\text{Im}\{\chi^{(3)}\}) / \text{esu}$	9.09×10^{-12}	9.30×10^{-12}	6.47×10^{-11}

5. Solid State Structure: Figure S4 shows the optical micrographs of crystal and fractal structures of the star compound **1-3** observed under crossed polarizers.

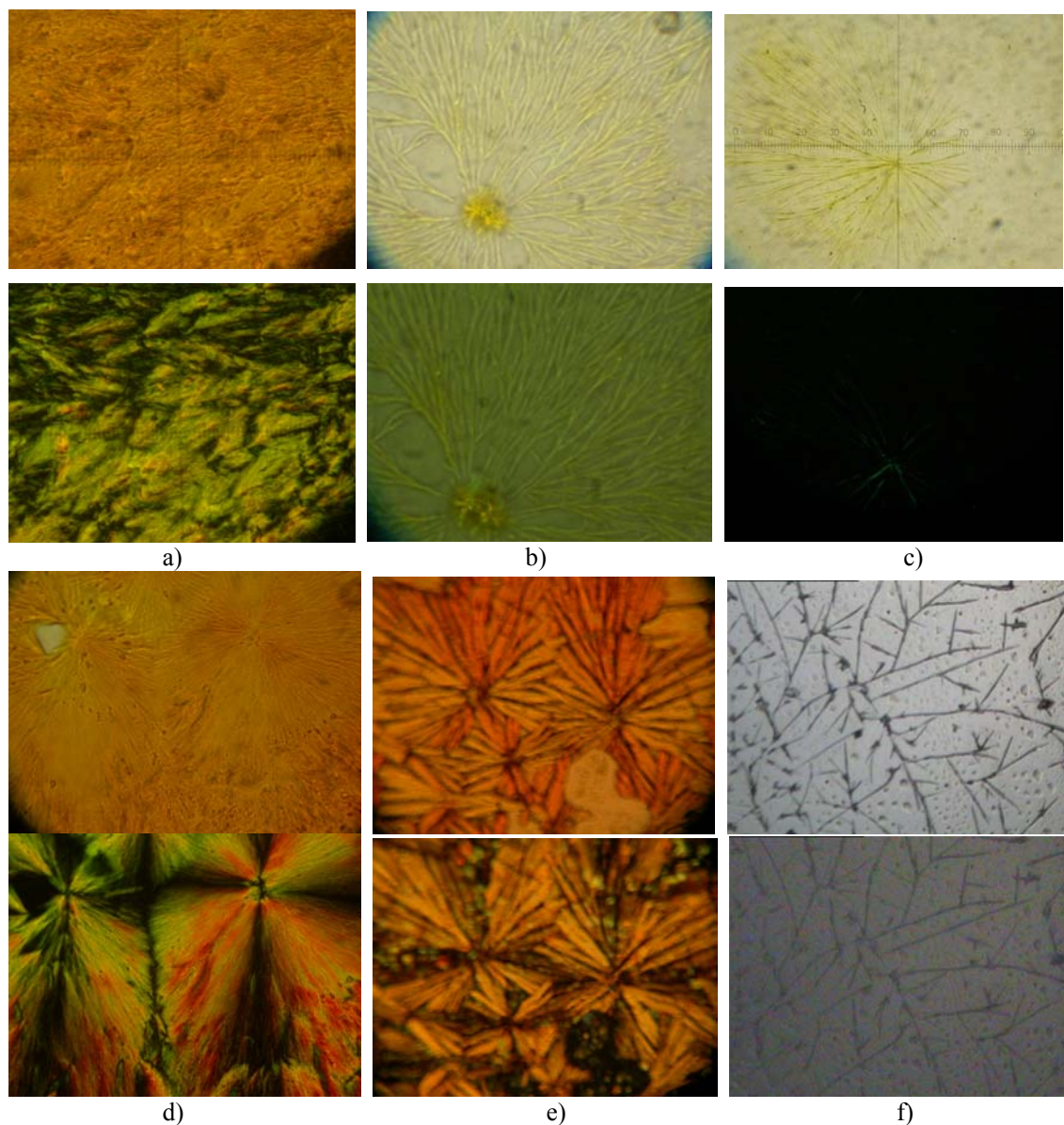


Figure S4. POM photographs of compound **1-3**. a): at saturated water solution of compound **1**; b) and c): spherulite micrograph from spin-coating membrane of compound **1** at 10 wt% DMF solution; d): compound **1** at saturated THF solution; e) micrograph as obtained by cooling from the isotropic melt (crossed polarizers) at room temperature of compound **2**; f) fractal structure of compound **3** at THF-Ether colloid solution

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