

Electronic Supplementary Information (ESI)

Rational design of light-directed dynamic spheres

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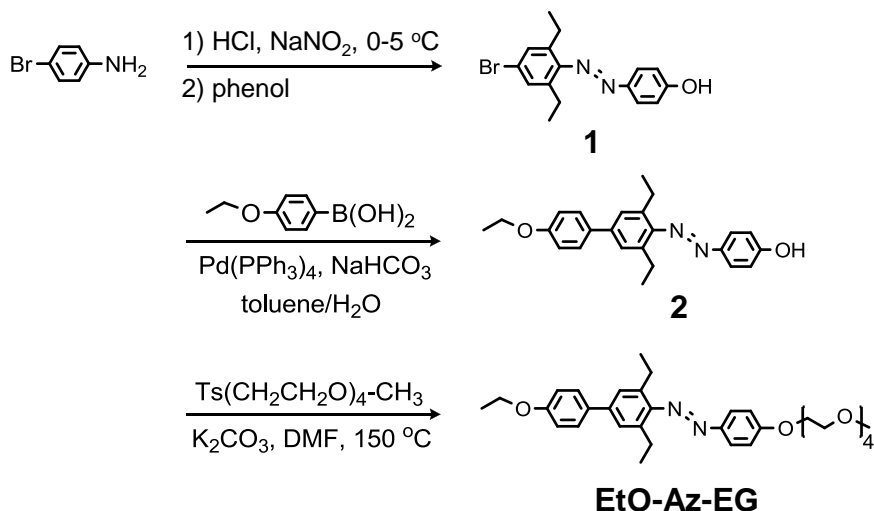
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Contents:

| | |
|------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 1. Synthesis | pS2 |
| 2. Instrumentation | pS3 |
| 3. Figure S1 DSC data: UV melts azobenzene | pS5 |
| 4. Figure S2 OM image of EtO-Az-EG spheres | pS5 |
| 5. Figure S3 DLS measurement of average size changes of azobenzene spheres | pS6 |
| 6. Figure S4 ¹ H NMR and UV-vis absorption spectral changes of EtO-Az-EG | pS6 |
| 7. Figure S5 UV-vis absorption spectral changes of azobenzene suspension | pS7 |
| 8. Figure S6 OM image of suspensions containing EtO-Az-EG and hydrophobic fluorescent dye DPA | pS7 |
| 9. Figure S7 DLS measurements of size changes of suspensions containing EtO-Az-EG and hydrophobic fluorescent dye DPA | pS8 |
| 10. Figure S8 UV-vis absorption spectral changes of suspensions containing EtO-Az-EG and DPA as a function of time of exposure to UV light | pS8 |
| 11. Figure S9 TEM image of suspensions containing EtO-Az-EG and DPA | pS9 |
| 12. Figure S10 DLS measurements of size changes of suspensions containing EtO-Az-EG and DPA | pS9 |

Synthesis of EtO-Az-EG

EtO-Az-EG was synthesized according to the following procedure.



4-[(E)-2-(4-bromo-2,6-diethylphenyl)diazen-1-yl]phenol (**1**)

A solution of NaNO₂ (1.27 g, 18.4 mmol) in H₂O/EtOH (10 mL/5 mL) was added to a solution of 4-bromo-2,6-diethylaniline (3.50 g, 15.4 mmol) and 1.6 M HCl (35 mL) at 0-5 °C. A solution of phenol (1.73 g, 18.4 mmol), NaOH (0.72 g, 18.4 mmol), and Na₂CO₃ (1.93 g, 18.4 mmol) in water (15 mL) was added to the diazonium salt solution. The mixture was stirred for 2 h at 0-5 °C, followed by the addition of water and ethyl acetate. The organic layer was separated and the solvent was removed from the reaction mixture by rotary evaporation. The residue was purified by silica gel column chromatography (hexane:ethyl acetate, v/v=20:1) to give an orange solid (4.19 g, yield: 82%).

¹H NMR (300MHz, CDCl₃) δ 1.12 (t, 6H, CH₃), 2.60 (q, 4H, CH₂), 5.53 (s, 1H, OH), 6.92 (d, J = 8.79 Hz, 2H, Ar-H), 7.26 (s, 2H, Ar-H), 7.82 (d, J = 9.06 Hz, 2H, Ar-H). ¹³C NMR (300MHz, CDCl₃) δ 15.2, 24.9, 115.9, 121.2, 124.7, 130.1, 138.4, 147.2, 150.1, 158.6.

(E)-4-((4'-Ethoxy-3,5-diethylbiphenyl-4-yl)diazenyl)phenol (**2**)

The compound (**2**) was prepared from the Suzuki coupling reaction of the precursor (**1**) in the presence of palladium(0) catalyst.^{1,2} A catalytic amount of tetrakis(triphenylphosphine)palladium(0) was added to the solution of the precursor **1** (6.44 g, 19.3 mmol) in toluene (60 mL). 4-Ethoxyphenylboronic acid (3.33 g, 20.0 mmol) and a solution of NaHCO₃ in distilled water (1N, 78 mL) were added to the above mixture. The reaction mixture was stirred at 100 °C for 7 h. After the mixture was cooled to room temperature, water and ethyl acetate were added. The organic layer was separated and purified by silica gel column chromatography (n-hexane:dichloromethane, v/v = 1/1) to

afford as an orange solid (4.93 g, yield: 64%).

^1H NMR (300MHz, CDCl_3) δ 1.11 (t, 6H, CH_3), 1.36 (t, 3H, CH_3), 2.65 (q, 4H, ArCH_2CH_3), 4.00 (q, 2H, $\text{ArOCH}_2\text{CH}_3$), 5.21 (s, 1H, OH), 6.93-6.97 (dd, $J = 8.52$ Hz, $J = 8.79$ Hz, 2H, Ar-H), 7.16 (s, 2H, Ar-H), 7.56 (d, $J = 8.52$ Hz, 2H, Ar-H), 7.86 (d, $J = 8.79$ Hz, 2H, Ar-H). ^{13}C NMR (300MHz, CDCl_3) δ 14.8, 15.6, 25.5, 63.6, 114.8, 115.8, 124.6, 125.9, 128.1, 133.4, 137.1, 140.4, 147.4, 149.7, 158.3, 158.5.

EtO-Az-EG: EtO-Az-EG was prepared by reacting the precursor (**2**, 1.26 g, 3.40 mmol) with 2,5,8,11-tetraoxatridecan-13-yl-4-methylbenzenesulfonate (1.44 g, 4.00 mmol) in N,N-dimethylformamide (20 mL) in the presence of K_2CO_3 (1.03 g, 7.44 mmol). The reaction mixture was stirred at 150 °C for 5 h and then cooled to room temperature, followed by the addition of water and ethyl acetate. The organic layer was collected and the solvent was removed by rotary evaporation. The residue was purified by silica gel column chromatography (hexane:dichloromethane, v/v = 1/1). (1.23 g, Yield: 64%).

^1H NMR (300 MHz, CD_2Cl_2) δ 1.19 (t, 6H, CH_3), 1.43 (t, 3H, CH_3), 2.76 (q, 4H, ArCH_2CH_3), 3.34 (s, 3H, $\text{ArO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$), 3.71-3.50 (m, 12H, $\text{ArOCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{OCH}_3$), 3.68 (t, 2H, $\text{ArOCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$), 3.80 (q, 2H, $\text{ArOCH}_2\text{CH}_3$), 4.15 (t, 2H, $\text{ArOCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$), 6.96-7.08 (dd, $J = 8.79$ Hz, 4H, Ar-H), 7.35(s, 2H, Ar-H), 7.58(d, $J = 8.52$ Hz, 2H, Ar-H), 7.87 (d, $J = 8.79$ Hz, 2H, Ar-H). ^{13}C NMR (300 MHz, CDCl_3) δ 14.85, 15.65, 25.50, 59.02, 63.53, 67.78, 67.78, 69.62, 70.53, 70.65, 70.90, 71.94, 114.73, 114.86, 124.29, 125.88, 128.10, 133.34, 137.11, 140.30, 147.44, 149.79, 158.57, 161.26. Anal. Calcd: C, 70.19; H, 7.85; N, 4.96. Found : C, 70.18; H, 7.70; N, 5.00. FAB-MS (m/z): $[\text{M} + \text{H}]^+$ found, 565.3299 (= M + 1), Calcd for $\text{C}_{33}\text{H}_{45}\text{N}_2\text{O}_6 = 565.3278$.

Instrumentation

Tetrahydrofuran (THF) of spectroscopic grade was used to dissolve EtO-Az-EG4. After a 30-sec nitrogen purge, a screw-cap quartz cuvette containing azobenzene solution was sealed with Parafilm[®]. Azobenzene suspensions were exposed to UV light (365 nm, Supercure-204S, Tokina, combination of Toshiba color filters, UV-35+UV-D36A) to induce trans-to-cis isomerization or visible light (436 nm, combination of Toshiba color filters, Y-43+V-44) to induce cis-to-trans isomerization. Absorption and fluorescence spectra were obtained using a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively. NMR spectra were obtained using JEOL JNM-ECP300 (300 MHz) spectrometers. The TEM (transmission electron microscope) sample was prepared by placing a drop of EtO-Az-EG suspension onto a carbon-coated copper grid and dried at ambient temperature. The TEM was performed at 100 kV using Hitachi H-7650 Zero A. Optical microscopic images were obtained using an Olympus BX51 optical microscope, after putting a few drops of EtO-Az-EG suspension on a clean glass substrate. Dynamic light

scattering measurements were recorded on a Sysmex Nano-ZS (Malvern Instruments Ltd) equipped with a He-Ne laser as the light source.

References

1. M. Han, D. Ishikawa, T. Honda, E. Ito and M. Hara, *Chem. Commun.*, 2010, **46**, 3598.
2. N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.

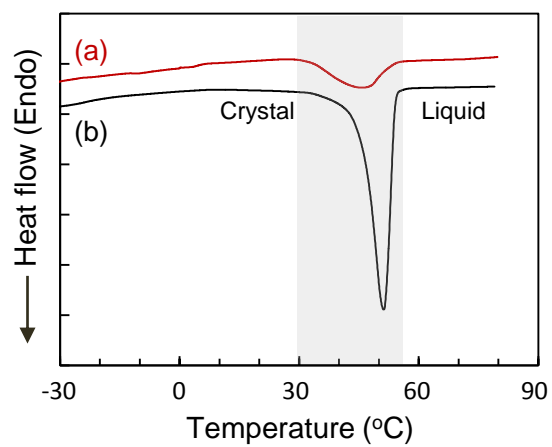


Figure S1. DSC thermograms observed for (a) cis-EtO-Az-EG and (b) trans-EtO-Az-EG.

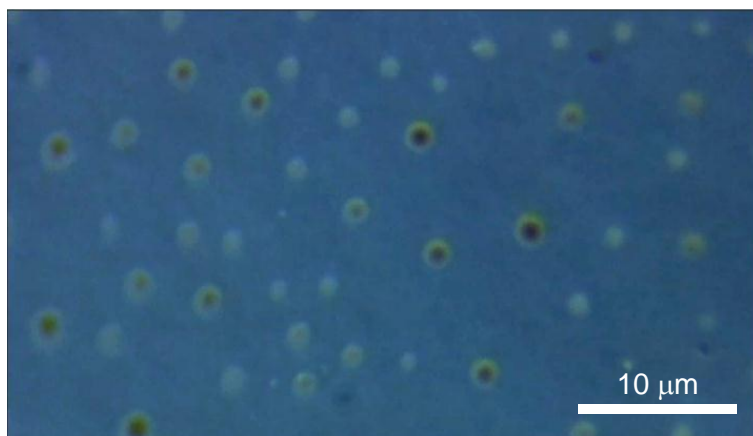


Figure S2. Optical microscopy image of EtO-Az-EG spheres prepared from 1.3×10^{-3} M THF/H₂O (4.0/8.2, v/v).

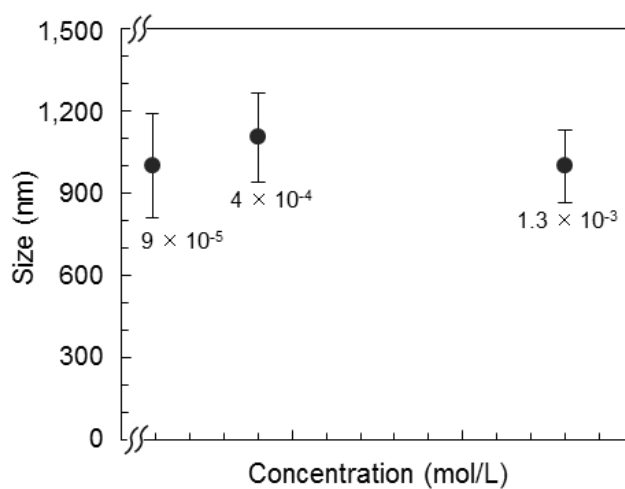


Figure S3. Dynamic light scattering results of azobenzene spheres prepared from various concentrations varying from 9.0×10^{-5} M to 4.0×10^{-4} and 1.3×10^{-3} M THF/H₂O suspensions.

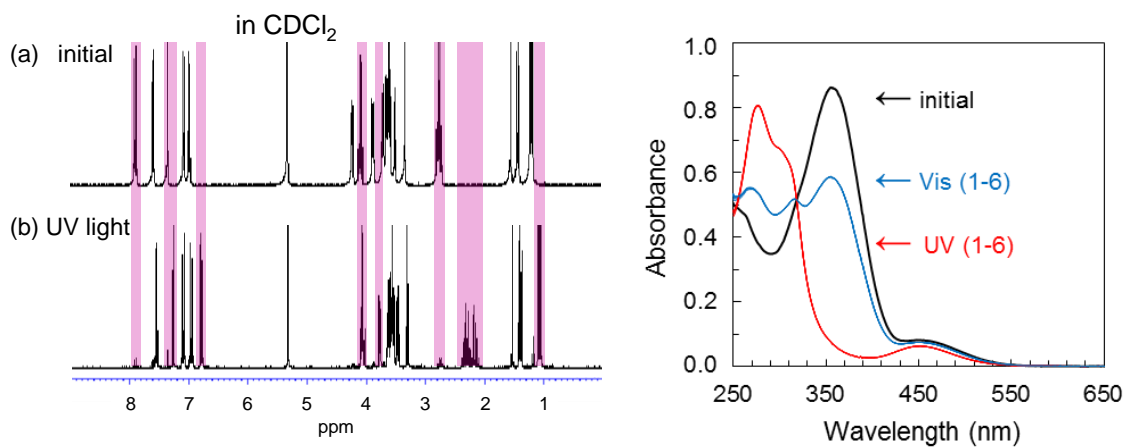


Figure S4. ¹H NMR (Left) and UV-vis absorption (Right) spectral changes of EtO-Az-EG.

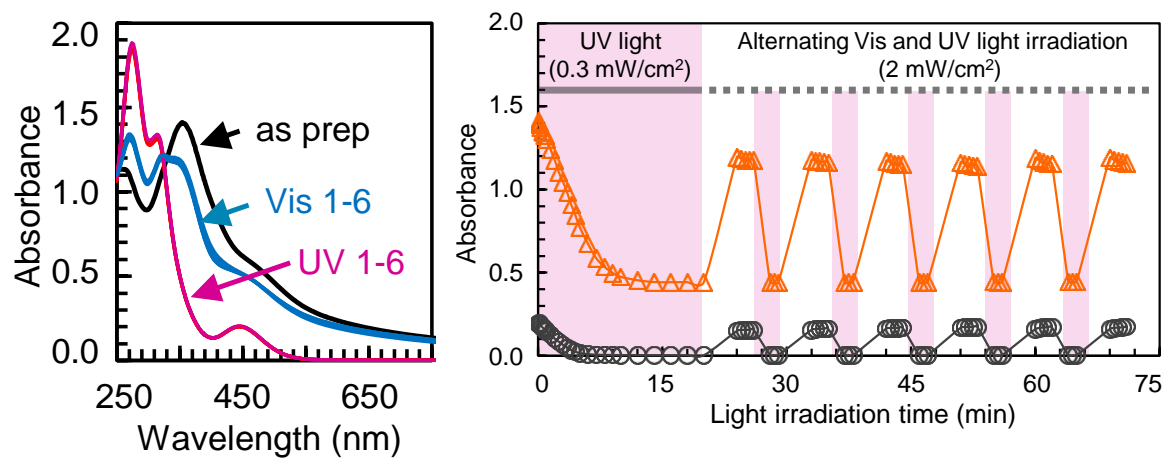


Figure S5. (Left) Absorption spectral changes of EtO-Az-EG (THF/H₂O = 2.0/7.0, v/v) suspension after alternating UV and visible light irradiation. (Right) Photoswitching: Changes in absorbance at 354 nm (triangle) and at 650 nm (circle).

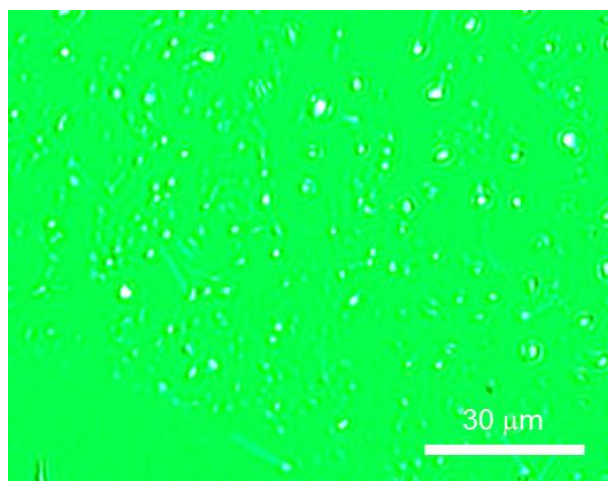


Figure S6. Optical microscopy image of aggregates containing EtO-Az-EG and hydrophobic fluorescent dye DPA.

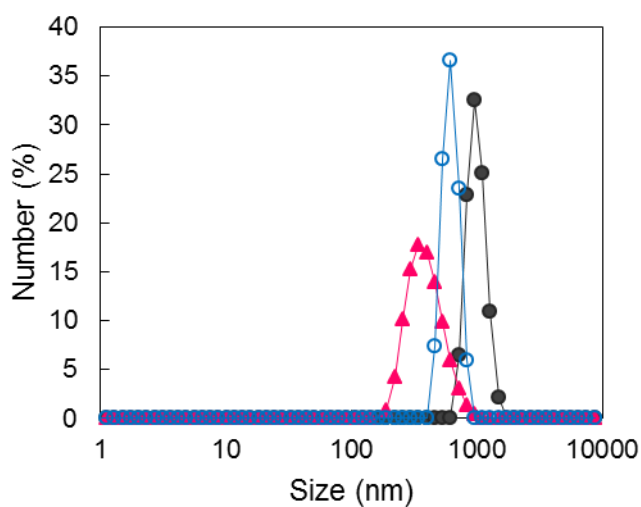


Figure S7. Dynamic light scattering results of suspensions containing EtO-Az-EG and hydrophobic fluorescent dye DPA upon alternating UV (triangle) and visible (open circle) light irradiation.

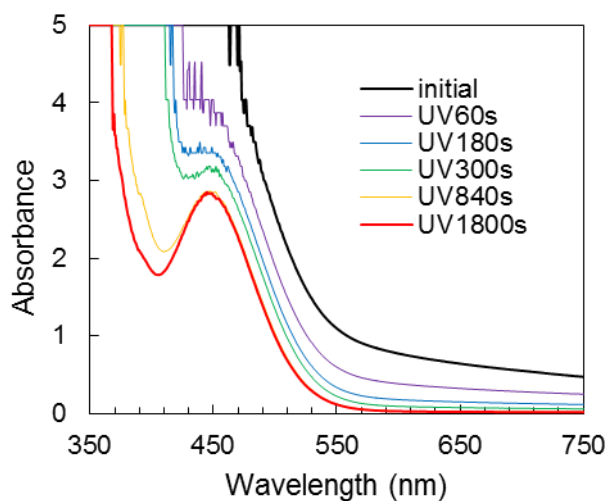


Figure S8. UV-vis absorption spectral changes of suspensions containing EtO-Az-EG (1.3×10^{-3} M) and hydrophobic fluorescent dye DPA (1.3×10^{-5} M) as a function of time of exposure to UV light.

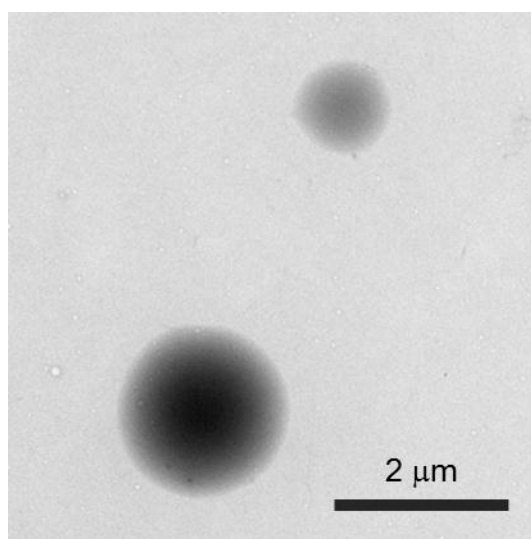


Figure S9. TEM image of suspensions containing EtO-Az-EG and hydrophobic fluorescent dye DPA.

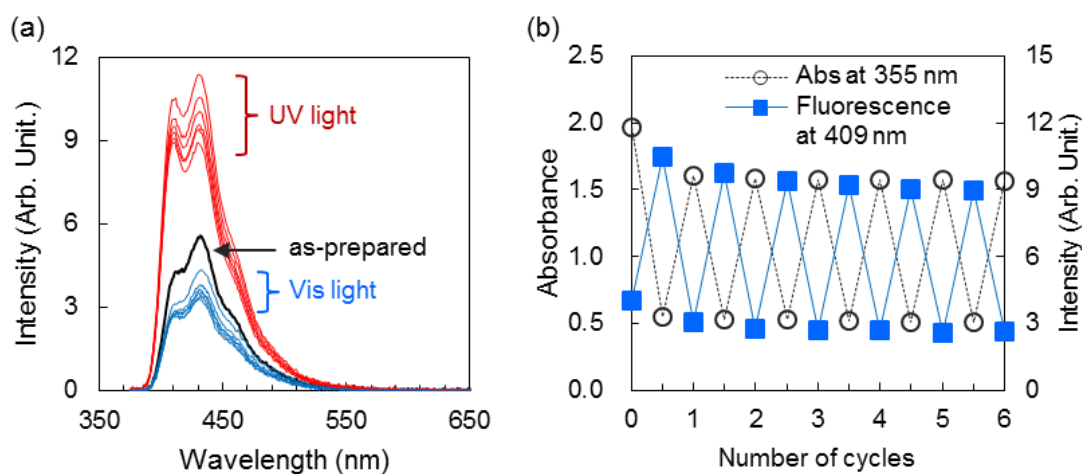


Figure S10. (a) Changes in fluorescence spectra upon alternating UV and visible light irradiation of suspensions containing EtO-Az-EG (9.4×10^{-5} M) and hydrophobic fluorescent dye DPA (1.9×10^{-5} M). (b) Changes in absorbance at 355 nm and fluorescence intensity at 409 nm as a function of exposure time of UV and visible light.