

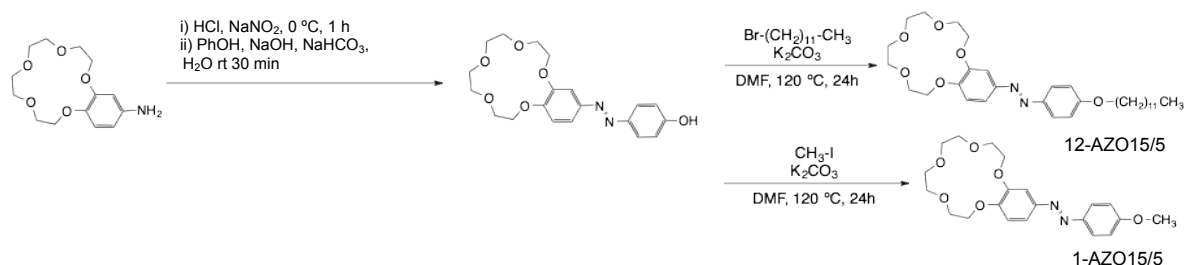
## SUPPORTING INFORMATION

### Chiral Supramolecular Organization from a Sheet-like Achiral Gel: Study of the Chiral Photoinduction

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#### Synthesis of gelators

**12-AZO15/5** and **1-AZO15/5** were synthesized according to a previously described procedure (Scheme S1).<sup>1</sup> All starting materials were purchased from commercial supplies and used as received.



**Scheme S1** Synthesis of **12-AZO15/5** and **1-AZO15/5**.

**4'-(p-Hydroxyphenylazo)benzo[15]crown-5 ether.** A solution of 4-aminobenzo[15]crown-5 ether (1.000 g, 3.53 mmol) in water (12 mL) was cooled into an ice/salt bath. Then, conc. HCl (0.65 mL) and  $\text{NaNO}_2$  (0.292 g, 4.24 mmol) were added to the solution and the mixture stirred for 1 h. A solution of NaOH (0.250 g, 6.25 mmol),  $\text{NaHCO}_3$  (0.125 g, 1.49 mmol) and phenol (0.399 g, 4.24 mmol) in water (2 mL) was added dropwise and the mixture was stirred for 1 h at room temperature. Orange crystals appeared that were isolated by filtration. The product was purified by recrystallization from ethanol/water to give 4'-(p-hydroxyphenylazo)benzo[15]crown-5 ether (1.654 g, 60% yield); mp  $141\text{ }^\circ\text{C}$ . FTIR (KBr disk,  $\text{cm}^{-1}$ ): 3181 (O–H), 1586, 1506 (C–C Ar), 1452 (N=N), 1262, 1117 (C–O).  $^1\text{H-NMR}$  [400 MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm), J (Hz)]: 7.70–7.68 (m, 2H), 7.50 (dd, 1H,  $J=8.4, 2.2$ ), 7.39 (d, 1H  $J=2.2$ ), 6.92 (d, 1H,  $J=8.4$ ), 6.87–6.84 (m, 2H), 4.24–4.17 (m, 4H), 3.99–3.90 (m, 4H), 3.82–3.75 (m, 8H).

**4'-(p-Dodecyloxyphenylazo)benzo[15]crown-5 ether (12-AZO15/5).** A solution of 1-bromododecane (0.389 g, 1.56 mmol) in *N,N*-dimethylformamide (5 mL) was added dropwise to a solution of 4'-(p-hydroxyphenylazo)benzo[15]crown-5 ether (0.500 g, 1.29 mmol),  $\text{K}_2\text{CO}_3$  (0.329 g, 2.60 mmol) and [18]crown-6 ether (70 mg, 0.26 mmol) in *N,N*-dimethylformamide (10 mL). The mixture was stirred at  $120\text{ }^\circ\text{C}$  for three days while monitoring its evolution by thin layer chromatography (dichloromethane/ethyl acetate 9:1). When the reaction was completed, water (50 mL) was added and the aqueous phase extracted with hexane/ethyl acetate 1:1 (3x50 mL). The combined organic extracts were dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by recrystallization from ethanol to yield orange crystals of 4'-(p-dodecyloxyphenylazo)benzo[15]crown-5 ether (90% yield, m.p.  $120.0\text{ }^\circ\text{C}$ ). FTIR (KBr,  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ ), 1595, 1502 (C–C Ar), 1467 (N=N), 1251, 1116 (C–O). 12-AZO15/5 ( $\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}_6$ )  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ), 7.89–7.82 (m, 2H), 7.51 (dd,  $J=8.4, 2.2$  Hz, 1H), 7.46 (d,  $J=2.2$  Hz, 1H), 7.01–6.93 (m, 3H), 4.29–4.16 (m, 4H), 4.03 (t,  $J=6.6$ , 2H), 3.98–3.90 (m, 4H), 3.83–3.74 (m, 8H), 1.92–1.70 (m, 2H), 1.58–1.14 (m, 18H), 0.88 (t,  $J=6.8$ , 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 161,23, 151,32, 149,41, 147,24, 146,80, 124,32, 120,01, 114,65, 112,54, 104,34, 71,21, 71,17, 70,40, 69,42 68,84, 68,75, 68,32, 31,90, 29,65, 29,62, 29,58, 29,56, 29,38, 29,34, 29,20, 26,01, 22,68, 14,11; HRMS (ESI+)  $m/z$  calcd: 601.3847 [ $\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}_6+\text{H}$ ] $^+$ ; found: 601.3926; elemental analysis calcd (%) for  $\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}_6$ : C 69.04, H, 8.69, N, 5.03; found: C 68.89, H 8.82, N 5.06.

4'-(*p*-Methoxyphenylazo)benzo[15]crown-5 ether (**1-AZO15/5**). This compound was prepared as described for 12-AZO15/5. 1-AZO15/5 (C<sub>21</sub>H<sub>27</sub>N<sub>2</sub>O<sub>6</sub>) (71% yield, m.p. 124 °C). FTIR (KBr,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ ), 1598, 1581 (C-C Ar), 1451 (N=N), 1247, 1116 (C-O) <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ), 7.89–7.83 (m, 2H), 7.55 (dd, *J*=8.5, 2.2, 1H), 7.46 (d, *J*=2.2, 1H), 7.04–6.95 (m, 2H), 6.96 (d, *J*=8.5, 1H), 4.25–4.17 (m, 4H), 3.96–3.92 (m, 4H), 3.88 (s, 3H), 3.78–3.76 (m, 8H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161,32, 151,36, 149,40, 147,19, 146,70, 124,38, 119,95, 114,72, 112,85, 104,74, 71,00, 70,85, 70,83, 70,79, 70,75, 69,56, 69,22, 69,07, 68,38, 31,92, 29,66, 29,63, 29,59, 29,57, 29,39, 29,34, 29,22, 26,03, 22,68, 14,10. HRMS (ESI+) *m/z* calcd: 403.1864 [C<sub>21</sub>H<sub>27</sub>N<sub>2</sub>O<sub>6</sub>+H]<sup>+</sup>; found: 403.1877;. elemental analysis calcd (%) for C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>: C 62.67, H 6.51, N 6.96. found: C 62.23, H, 6.46, N, 6.96.

## Instruments and methods

IR spectra were obtained from KBr pellets using a Nicolet Avatar 360-FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were measured on a Bruker AV-400 spectrometer. Mass spectra were measured on a Bruker Micro-TOF-Q mass spectrometer. Elemental analysis was performed on a Perkin-Elmer 240C microanalyzer. Gel-like samples were inspected by polarizing optical microscopy (POM) using an Olympus BH-2 polarizing microscope. The samples for POM inspection were prepared *in situ* from a droplet of the warm solution deposited on a glass slide at room temperature, where gel formation occurred. Scanning electron microscopy (SEM) was performed on a Hitachi S2300 instrument. The gels were dropped onto a glass surface and the excess solvent was removed by capillarity using absorbent paper. The dry samples (xerogels) were covered with a thin Au layer and were placed on a conductor surface for their observation. Cryogenic scanning electron microscopy (cryo-SEM) was performed using a Dual Beam 3 Nova 200 microscope. The gels were frozen in liquid nitrogen and fractured. The fracture was covered with a thin Pt layer prior to observation. Atomic force microscopy (AFM) was carried out using a Veeco-Bruker Multimode 8 in intermittent contact mode (tapping) with a silicon tip (resonance frequency 380 kHz). The mean minimum thickness of the nanosheets was determined by measuring the profile in height, z-axis, of an arbitrary direction, defined in the xy-plane, perpendicular to the surface of the nanosheets. The roughness of the surface was defined as the quotient between the real and geometric surfaces. The actual surface area of the nanosheets was measured by AFM, with the variations recorded in height, z-axis, on a surface of 100 nm<sup>2</sup>, xy plane, and calculating the value of the mean square roughness (*R*<sub>RMS</sub>). The measurements of the xerogel-water contact angle were performed with a Theta Lite optical tensiometer from Attension and Milli-Q water was used. The xerogel, prepared in the same way as described for the SEM study, was deposited on a glass surface. Water was then deposited on the xerogel surface. The continuity of the xerogel film was checked by POM. The results were adjusted with the Young–Laplace equation, which allows measurement between 0° and 180° with an accuracy of 0.1°.

### Gel formation and gel-sol transition temperature

Gel formation was evaluated by the ‘inversion of a test tube’ method.<sup>2</sup> A weighed amount of gelator and a measured volume of the test solvent were placed in a screw-sealed vial and the mixture was heated on a hot plate until the solid had dissolved. The resulting clear solution was then cooled to room temperature and the sample was inverted to determine whether flow was possible. Initially the concentration of gelator studied was 5.0% wt. When a soft state was formed the concentration was subsequently decreased to 2.5% wt, 1% wt and 0.5% wt in order to determine the minimum gelation concentrations at room temperature. The gel-sol transition temperature (*T*<sub>gel</sub>) was measured by the falling sphere test. A controlled amount of material (400 mg) was placed in a 10 mm diameter sealed vial and one lead sphere (1 mm diameter) was added. The vial was immersed in a small amount (100 mL) of silicon oil with a magnetic stirrer and placed on a hot plate. The temperature ramp was adjusted to 1 °C/min. The temperature when the lead sphere fell to the bottom of the vial was defined as the sol-gel transition temperature.

### Crystal structure analysis

X-ray diffraction patterns for gels and polycrystalline samples were collected on a Bruker D8 Advance diffractometer equipped with a Cu tube, Ge(111) incident beam monochromator ( $\lambda=1.5406 \text{ \AA}$ ) and a Sol-X energy dispersive detector. The sample was measured as a continuous scan in locked coupled mode. Data were collected from 1 to 60° 2 $\theta$  (step size=0.03 and time per step=20 s) at room temperature. A variable divergence and antiscattering slit *V*<sub>6</sub> giving a constant sample illumination area was used. The sample was gelled *in situ* on the surface of the diffraction cell using a heated solution. X-ray quality single crystals were obtained by slow evaporation of solution **1-AZO15/5** in CH<sub>3</sub>CN. The crystals were air stable and were mounted on the tip of a glass fiber. X-ray diffraction experiments were carried out on an Oxford-diffraction Xcalibur S diffractometer. Data were collected at 293(2) K with Mo–K $\alpha$  radiation. Software packages XSCANS<sup>3</sup> and CrysAlis<sup>4</sup> were used to process data. Final cell parameters were obtained by global refinement of reflections obtained from integration of all the frames data. The structures were solved by direct methods and refined by the full-matrix method based on *F*<sup>2</sup> using the

SHELXTL program.<sup>5</sup> The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were observed in difference electron density maps and refined isotropically.

#### **Photoresponsive properties**

To investigate the photoresponse of the materials, the gel was placed between two quartz plates and the optical pathlength was adjusted in each case with Teflon<sup>®</sup> separators to obtain a maximum absorbance of 1.5. UV-vis and ECD spectra of the gels were registered using a Jasco J-810 spectropolarimeter 5 minutes after irradiation. The ECD spectra of the films were registered by rotating the samples in 60 degree intervals around the light beam axis in order to check that the contribution of linear dichroism to ECD spectra was negligible. Irradiation with UV light was carried out using an Hg lamp (1000 W, Oriel) and a 365 nm filter (power 29 mW/cm<sup>2</sup>). Irradiation with visible light was carried out using the 488 nm line of an Ar<sup>+</sup> laser (power 25 mW/cm<sup>2</sup>).

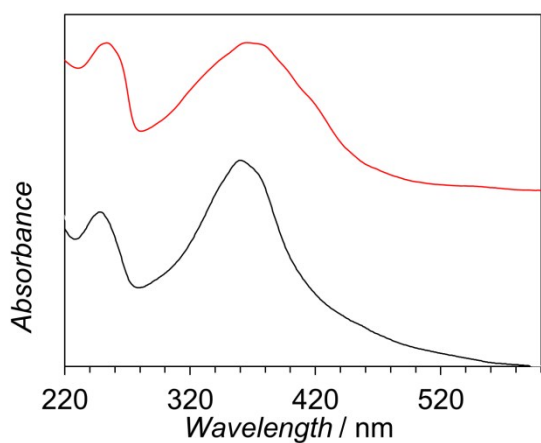
#### **DFT calculations**

To support the discussion, DFT and TD-DFT calculations were performed using the Gaussian 09 suite of programs.<sup>6</sup> Geometry optimizations were carried out *in vacuo* with the B3LYP method<sup>7-9</sup> with the van der Waals dispersion corrections,<sup>10</sup> employing 6-31G\*<sup>11</sup> for all atoms and carried out without constraints, using the default convergence criteria for the Gaussian software. UV and ECD spectra were calculated using TD-DFT calculations at the same functional and basis set level. In order to obtain more in-depth data on the conformational behavior of the gelators, the angle between the aromatic rings ( $\phi_1$ ) was selected and varied from the value for the optimized conformer every 1° from the initial angle over 18°. In every step, the total energy of the corresponding conformer was calculated by single-point calculation on the computed potential energy surface. In addition, UV and ECD for these conformers were calculated using TD-DFT at the same functional and basis set level.

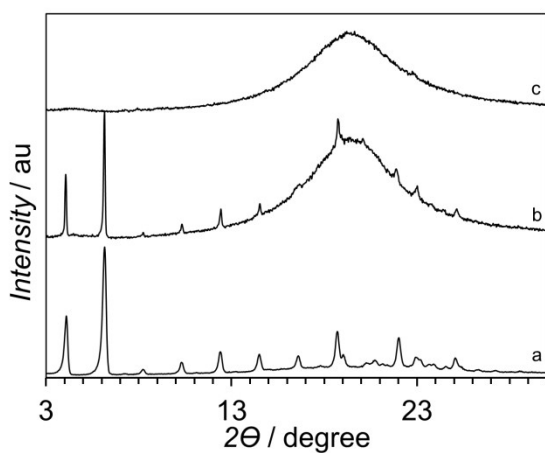
**Table S1** Gelation properties of **12-AZO15/5** and **1-AZO15/5** at room temperature<sup>a)</sup>

Solvent	12-AZO15/5	1-AZO15/5
Hexane	I	I
Dodecane	G(5.0)	G(5.0)
Cyclohexane	I	I
Toluene	I	S
Chloroform	S	S
Tetrahydrofuran	I	S
Water	I	I
Methanol	G(5.0)	I
Ethanol	G(5.0)	I
<i>terc</i> -Butanol	G(2.5)	I
Isopropanol	G(2.5)	I
1-Butanol	G(2.5)	I
1-Hexanol	I	I
1-Nonanol	G(5.0)	I
1-Decanol	G(5.0)	I
1-Dodecanol	G(2.0)	G(5.0)

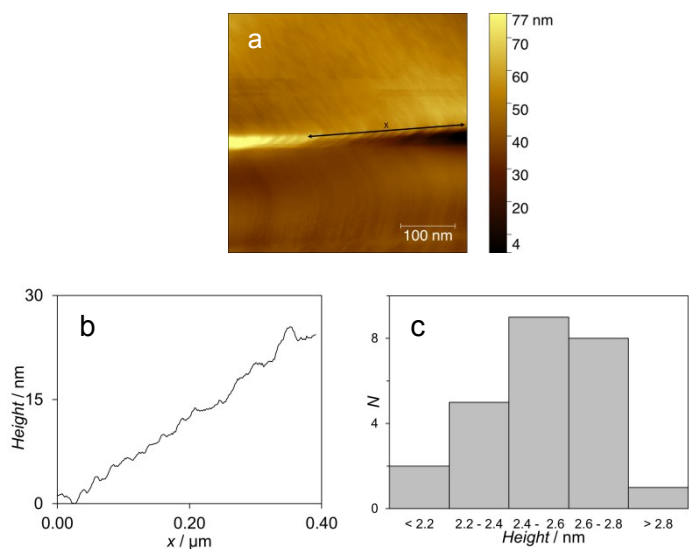
<sup>a)</sup>G: gel; S: soluble; I: insoluble. For gels, the minimum gelation concentration (MGC) at room temperature in brackets (% wt).



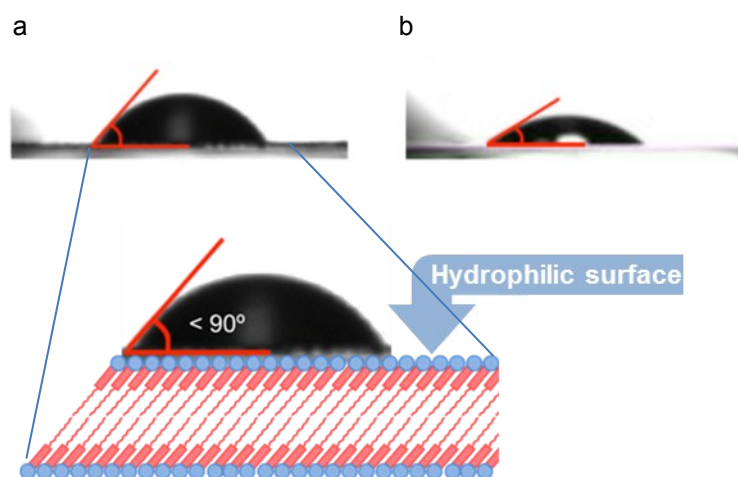
**Fig. S1** Absorption spectra of fibrillar gel G(12-AZO15/5-2.0) (–) and sheet-like gel G(12-AZO15/5-6.0) (–).



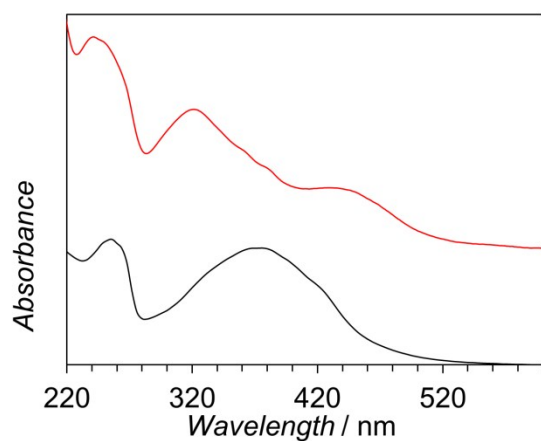
**Fig. S2** Powder XRD diagrams of a) polycrystalline **12-AZO15/5**; b) G(12-AZO15/5)-6.0 and c) G(12-AZO15/5)-2.0.



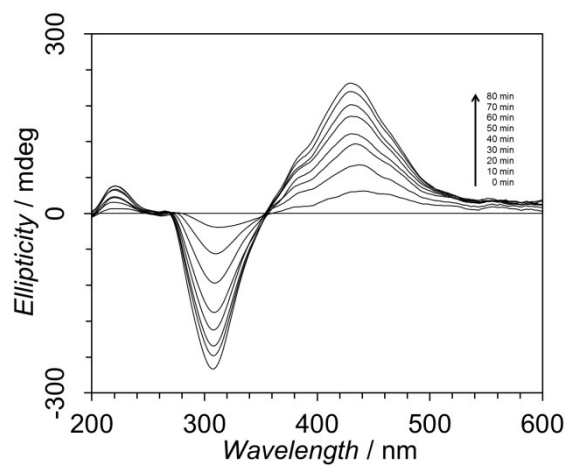
**Fig. S3** AFM data of xerogel from G(1-AZO15/5) 5.0: (a) AFM height image; (b) cross section profiles of xerogel, and (c) step height distribution histograms.



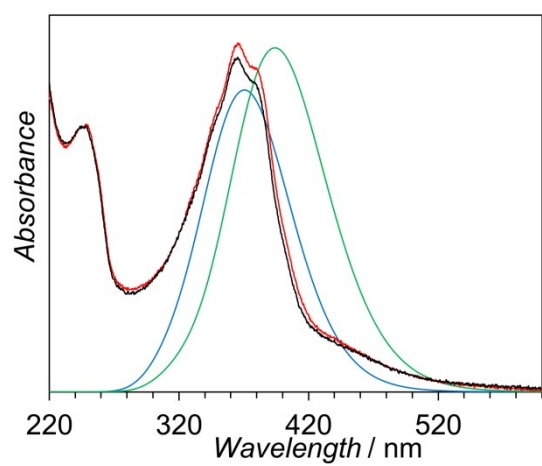
**Fig. S4** Water contact angle of xerogel from G(12-AZO15/5)-6.0 (a) and glass (b).



**Fig. S5** Absorption spectra of G(12-AZO15/5)-6.0 after irradiation with circular polarized light for 80 min, 488 nm line, 25 mW/cm<sup>2</sup> (—) and for 30 min, 365 nm, 29 mW/cm<sup>2</sup> (---).



**Fig. S6** ECD spectra of G(12-AZO15/5)-6.0 after irradiation with 488 nm *r*-CPL.



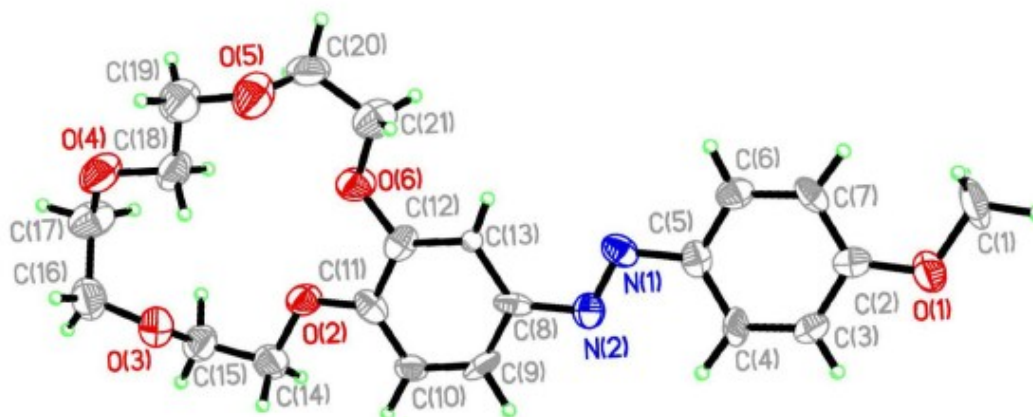
**Fig. S7** Absorption spectra in 1-dodecanol solutions of **1-AZO15/5** (—) and **12-AZO15/5** (—). Calculated absorption spectrum of the enantiomer of the crystal structure of **1-AZO15/5** in vacuum (—) and in 1-octanol solution (PCM approach) (—). TD-B3LYP-D3-31G(d) level with Gaussian 09.<sup>6</sup>

## Crystallography

X-ray quality single crystals were obtained by slow evaporation of solution **1-AZO15/5** in CH<sub>3</sub>CN. The crystals are air stable and were mounted on the tip of a glass fibre. X-ray diffraction experiments were carried out on an Oxford-diffraction Xcalibur S diffractometer. Data were collected at 293(2) K with Mo-K $\alpha$  radiation. Software packages XSCANS<sup>12</sup> and CrysAlis<sup>13</sup> were used to process data.

Final cell parameters were obtained by global refinement of reflections obtained from integration of all the frames data. The structures were solved by direct methods and refined by the full-matrix method based on F<sup>2</sup> using the SHELXTL program.<sup>14</sup> The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were observed in difference electron density maps and refined isotropically (**Figure S8**). The crystal parameters and basic information relating data collection and structure refinement are summarized in **Table S2**.

Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC 1516204. Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Fig. S8** The molecular structure and scheme numbering of **1-AZO15/5** with displacement ellipsoids drawn at the 50% probability level.

**Table S2** Crystallographic data for **1-AZO15/5**.

Compound	<b>1-AZO15/5</b>
Empirical formula	C <sub>21</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub>
Formula weight	402.44
Crystal System	Monoclinic
a, Å	23.191(8)
b, Å	5.2256(13)
c, Å	16.932(5)
α, deg	
β, deg	98.63(3)
γ, deg	
V, Å <sup>3</sup>	2028.7(11)
T, K	293(2)
Space group	P2 <sub>1</sub> /c
Z	4
μ(Mo Kα), mm <sup>-1</sup>	0.097
θ range, deg	3.22 to 25.00
Refl. collected	14776
Uniq reflect / Rint	3560 / 0.2691
R1 <sup>a</sup> /wR2 <sup>b</sup> (I>2σ)	0.1137 / 0.1342
R1 <sup>a</sup> /wR2 <sup>b</sup> (all data)	0.3147 / 0.1852
Max. shift/esd	0.001
Residual ρ/e Å <sup>-3</sup>	0.225 and -0.205



**Table S3** Calculated gas-phase energy of **12-AZO15/5** optimized with B3LYP-D3/6-31G-d and Cartesian coordinates of calculated structure.

12-AZO15/5, Energy = -1809.234794 Hartrees

O	-3.569384	-1.815543	0.21827
N	1.912792	-0.930591	-0.160923
C	-4.499022	-0.747631	0.042643
H	-4.367471	-0.300492	-0.953202
H	-4.311231	0.03588	0.790828
O	8.139774	-0.983178	-0.405587
N	2.673168	-1.930702	-0.013714
C	-2.241652	-1.543608	0.116171
C	-1.380713	-2.643924	0.294186
H	-1.824841	-3.613296	0.497308
O	10.672128	-0.558772	0.808845
C	-0.011415	-2.482342	0.210266
H	0.662196	-3.320689	0.344997
O	10.818246	2.471117	0.398963
C	0.536429	-1.210857	-0.054244
O	7.339384	3.500445	0.633354
C	-0.324799	-0.123377	-0.228046
H	0.113787	0.848947	-0.429855
O	6.547748	1.034083	-0.642098
C	-1.707383	-0.276027	-0.146388
H	-2.351058	0.583825	-0.285634
C	4.048947	-1.645435	-0.11731
C	4.912918	-2.729084	0.024819
H	4.489952	-3.711454	0.205199
C	6.294791	-2.545119	-0.06557
H	6.955999	-3.395549	0.047907
C	6.818689	-1.274683	-0.295767
C	5.93886	-0.164739	-0.43255
C	4.571631	-0.355625	-0.347941
H	3.871712	0.462234	-0.452328
C	9.0803	-2.022033	-0.170843
H	8.959843	-2.824352	-0.91267
H	8.939208	-2.444005	0.832593
C	10.461421	-1.418634	-0.290812
H	11.211928	-2.227544	-0.300307
H	10.531204	-0.88378	-1.248523
C	11.834688	0.24983	0.695906
H	12.68319	-0.345726	0.317255
H	12.072524	0.576397	1.71302
C	11.644167	1.486073	-0.180863
H	12.62443	1.957933	-0.323708
H	11.2641	1.200816	-1.175693
C	9.415596	2.222047	0.336987
H	9.09287	1.503673	1.097574
H	9.137617	1.799781	-0.638413
C	8.753454	3.579431	0.563938
H	9.084767	3.981083	1.526415
H	9.076705	4.282963	-0.217954
C	6.667354	3.403577	-0.609407
H	7.374116	3.316515	-1.444936
H	6.065422	4.310976	-0.769377
C	5.741009	2.204323	-0.606457
H	5.128754	2.214518	0.304128
H	5.072004	2.235077	-1.479096
C	-5.89984	-1.316052	0.197052
H	-6.037617	-2.117966	-0.539055
H	-5.986072	-1.778682	1.188184
C	-6.979565	-0.244599	0.018669
H	-6.875007	0.220832	-0.972165
H	-6.823714	0.560112	0.751762
C	-8.400931	-0.794896	0.169247
H	-8.507664	-1.258776	1.16033
H	-8.55743	-1.600497	-0.56245
C	-9.48306	0.273216	-0.01153
H	-9.373129	0.737448	-1.002521
H	-9.324264	1.078826	0.720181
C	-10.906729	-0.271233	0.136771
H	-11.065582	-1.077251	-0.594428
H	-11.017593	-0.734602	1.127996
C	-11.986927	0.798711	-0.046112
H	-11.874522	1.262436	-1.037097
H	-11.827521	1.604499	0.685323
C	-13.412005	0.257447	0.100324

H	-13.571474	-0.548485	-0.630915
H	-13.525026	-0.205768	1.09144
C	-14.490658	1.328767	-0.083857
H	-14.3765	1.792353	-1.074748
H	-14.331027	2.134399	0.647763
C	-15.916495	0.789309	0.060997
H	-16.07687	-0.01634	-0.670613
H	-16.031616	0.325804	1.051928
C	-16.995197	1.861078	-0.123666
H	-16.87846	2.323952	-1.113658
H	-16.834865	2.66491	0.60857
C	-18.416465	1.311881	0.021392
H	-19.167597	2.09827	-0.113304
H	-18.614566	0.529542	-0.721431
H	-18.568901	0.87033	1.013836

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