Supplementary Information

Light-driven nanofiber and nanoring morphological transformations in organogels based on an azobenzene-bridged biscalix[4]arene

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Materials and Methods

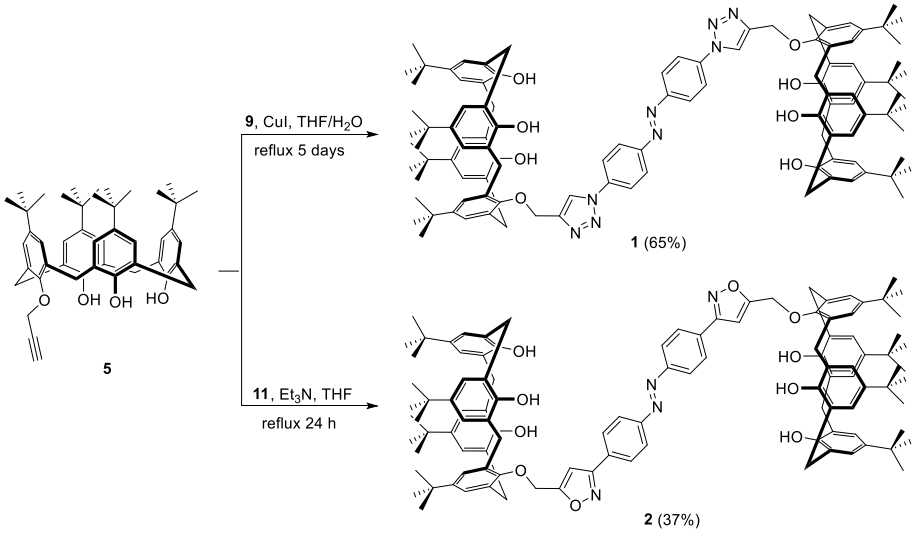
All other chemical reagents were commercially available and were used without further purification unless otherwise noted. Compounds **5**[S1], **6**[S2], **7**[S3] and **8**[S4] were synthesized according to literature methods.

S1. C.-C. Tsai, K.-C. Chang, I.-T. Ho, J.-H. Chu, Y.-T. Cheng, L.-C. Shen, W.-S. Chung, *Chem. Commun.*, 2013, **49**, 3037–3039.

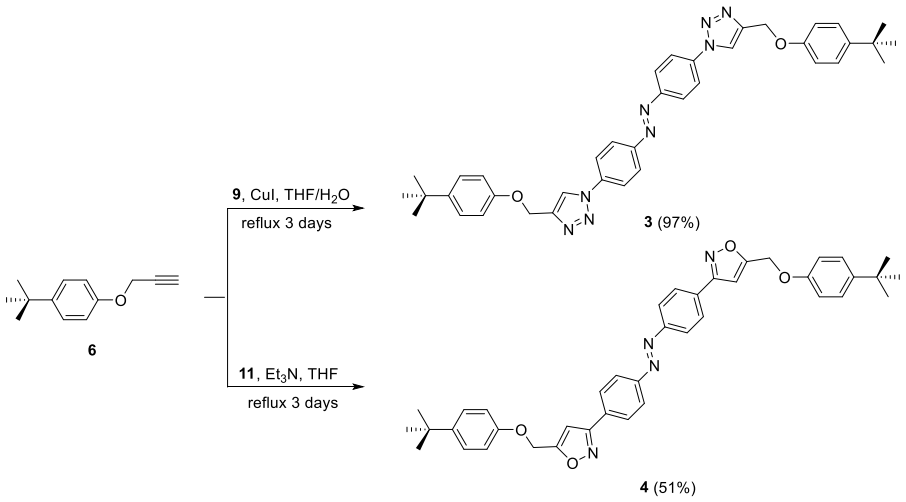
S2. Y. Wang, K. Ji, S. Lan, L. Zhang, *Angew. Chem., Int. Ed.*, 2012, **51**, 1915–1918.

S3. L. Hamryszak, H. Janeczek, E. Schab-Balcerzak, *J. Mol. Liq.*, 2012, **165**, 12–20.

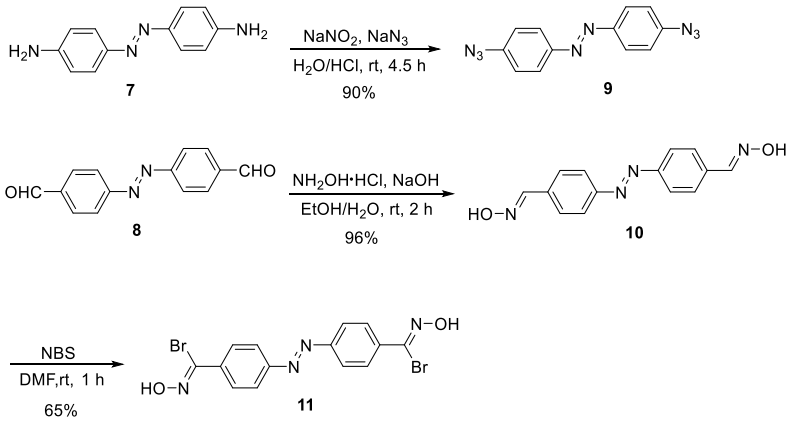
S4. L. Masciello, P. G. Potvin, *Can. J. Chem.*, 2003, **8**, 209–218.



Scheme S1. Syntheses of biscalix[4]arenes **1** and **2**.



Scheme S2. Syntheses of control compounds **3** and **4**.



Scheme S3. Syntheses of the azobenzene derivatives **9** and **11**.

Biscalix[4]arene 1: A solution of **5**[S1] (0.37 g, 0.53 mmol) in THF (27 mL) and water (1 mL) was treated with CuI (0.005 g, 0.026 mmol) and 4,4'-diazidoazobenzene **9** (0.07 g, 0.27 mmol), and the resulting mixture was stirred and heated at reflux for 5 d. After reaction, the volatile solvent was removed under reduced pressure. Subsequently, water (100 mL) was added and the suspension was extracted with CH_2Cl_2 (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford the crude reaction mixture, which was purified by silica-gel column chromatography (ethyl acetate/*n*-hexane = 1/4) to afford 287 mg (65% yield) of product **1** as an orange solid. R_f = 0.30 (ethyl acetate/*n*-hexane = 1/4); mp 205-206 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 10.11 (s, 2H), 9.41 (s, 4H), 8.93 (s, 2H), 8.21 (d, J = 8.8 Hz, 4H), 8.11 (d, J = 8.8 Hz, 4H), 5.44 (s, 4H), 4.46 (d, J = 13.1 Hz, 4H), 4.24 (d, J = 13.7 Hz, 4H), 3.51 (d, J = 13.1 Hz, 4H), 3.44 (d, J = 13.7 Hz, 4H), 1.22-1.20 ppm (m, 72H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1 (Cq), 148.9 (Cq), 148.8 (Cq), 148.2 (Cq), 147.5 (Cq), 144.5 (Cq), 143.8 (Cq), 143.4 (Cq), 138.8 (Cq), 133.5 (Cq), 128.2 (Cq), 127.9 (Cq), 127.5 (Cq), 126.7 (CH), 125.8 (CH), 125.8(CH), 125.7 (CH), 124.7 (CH), 122.1 (CH), 121.1 (CH), 69.9 (CH_2), 34.3 (Cq), 34.0 (Cq), 33.9 (Cq), 33.0 (CH_2), 32.3 (CH_2), 31.5 (CH_3), 31.4 (CH_3), 31.2 (CH_3) ppm; HRMS *m/z* calcd for $C_{106}H_{124}N_8NaO_8$ [M + Na^+] 1659.9434; found 1659.9404.

X-ray single crystal data for compund 1: $C_{106}H_{124}N_8O_8$, M = 1638.12, monoclinic, a = 36.5263 (18) Å , b = 14.3181(3) Å , c = 26.3568(11) Å , α = 90°, β = 110.445(5)°, γ = 90°, V = 12916.0(10) Å ^{3}, space group $C2/c$; Z = 4, ρ_{calcd} = 0.842 Mg/m^3, crystal dimensions (mm^3): 0.25 × 0.20 × 0.15, T = 200(2) K, λ ($Cu_{K\alpha}$) = 1.54178 Å , 23477 reflections collected; 11734 independent reflections [R(int) = 0.0372]; μ = 0.416 mm^{-1}, 641 parameter refined on F^2, R_1 = 0.0719, wR_2 = 0.2133 (all data), goodness-of-fit (GOF) on F^2 = 1.331, $\Delta\rho_{max}$ = 0.297 eÅ $^{-3}$. CCDC 1573644 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_ -request/cif.

Biscalix[4]arene 2: A solution of **5**[S1] (0.09 g, 0.13 mmol) in THF (5 mL) was treated with hydroximoyl bromide **11** (0.03 g, 0.06 mmol) under nitrogen atmosphere, then the solution of triethylamine (0.04 mL, 0.25 mmol) in THF (1 mL) was added dropwise over a period of 5 min. The mixture was stirred at reflux for 24 hr. After cool to room temperature, the volatile solvent was removed under reduced pressure. Subsequently, water (100 mL) was added and the suspension was extracted with CH_2Cl_2 (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford the crude reaction mixture, which was purified by silica-gel column chromatography (ethyl acetate/*n*-hexane = 1/3) to afford 40 mg (37%) of product **2** as an orange solid. R_f = 0.28 (ethyl acetate/*n*-hexane = 1/3); mp 198-200 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 10.01 (s, 2 H), 9.16 (s, 4 H), 8.11-8.08 (m, 8 H), 7.16 (s, 2 H), 7.13 (s, 4 H), 7.07 (d, J = 2.0 Hz, 4 H), 7.05 (s, 4 H), 7.00 (d, J = 2.0 Hz, 4 H), 5.41 (s, 4 H), 4.35 (d, J = 13.2 Hz, 4 H), 4.27 (d, J = 13.7 Hz, 4 H), 3.48-3.44 (m, 8 H), 1.22-1.21 (m, 72 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7 (Cq), 162.1 (Cq), 153.5 (Cq), 149.0 (Cq), 148.9 (Cq), 148.3 (Cq), 147.5 (Cq), 143.7 (Cq), 143.3 (Cq), 133.3 (Cq), 131.3 (Cq), 128.2 (Cq), 127.9 (CH), 127.7 (Cq), 127.5 (Cq), 126.8 (CH), 125.9 (CH), 125.7 (CH), 125.6 (CH), 123.7 (CH), 102.9 (CH), 68.2 (CH_2), 34.3 (Cq), 34.0 (Cq), 33.9 (Cq), 32.9 (CH_2), 32.2 (CH_2), 31.5 (CH_3), 31.4 (CH_3), 31.2 (CH_3) ppm; HRMS *m*/*z* calcd for $C_{108}H_{124}N_4NaO_{10}$ [M + Na^+] 1659.9210; found, 1659.9169.

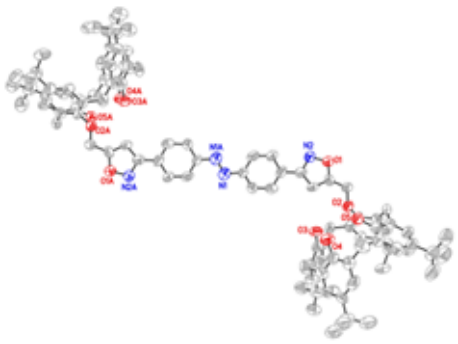


Fig. Sa X-ray single crystal structure of bis-isoxazolylazobenzene bridged biscalix[4]arene **2**.

X-ray single crystal data for compund 2: $C_{112}H_{128}Cl_{12}N_4O_{10}$, M = 2115.58, triclinic, a = 36.231(3) Å, b = 14.2891(9) Å, c = 26.170(3) Å, α = 90°, β = 109.636(11)°, γ = 90°, V = 12761(2) $Å^3$; space group *C*2/*c*, Z = 4, ρ_{calcd} = 1.101 Mg/m^3, crystal dimensions (mm^3): 0.25 × 0.15 × 0.10, T = 200(2) K, λ ($Mo_{K\alpha}$) = 0.71073 Å, μ = 0.311 mm^{-1}, 18821 reflections collected; 18821 independent reflections [*R*(int) = 0.0000], 785 parameter refined on F^2, R_1 = 0.1561, wR_2 [F^2] = 0.3765 (all data), goodness-of-fit (GOF) on F^2 1.784; $\Delta\rho_{max}$ = 0.876 $eÅ^{-3}$. CCDC 1573141 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center vis www.ccdc.cam.ac.uk/data_-request/cif.

Compound 3. A solution of **6**[S2] (0.42 g, 2.38 mmol) in THF (31 mL) and water (1 mL) was treated with CuI (0.03 g, 0.16 mmol) and 4,4'-diazidoazobenzene **9** (0.3 g, 1.14 mmol), and the resulting mixture was stirred and heated at reflux for 3 days. After reaction, the volatile solvent was removed under reduced pressure. Subsequently, water (100 mL) was added and the suspension was extracted with CH_2Cl_2 (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford the crude reaction mixture, which was washed with MeOH and collected by filtration to give 700 mg (97% yield) of product **3** as an orange solid. Mp 291-293 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 2 H), 8.13 (d, *J* = 8.8 Hz, 4 H), 7.96 (d, *J* = 8.8 Hz, 4 H), 7.34 (d, *J* = 8.8 Hz, 4 H), 6.98 (d, *J* = 8.8 Hz, 4 H), 5.32 (s, 4 H), 1.32 (s, 18 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9 (Cq), 152.0 (Cq), 145.8 (Cq), 144.2 (Cq), 138.7 (Cq), 126.4 (CH), 124.6 (CH), 121.0 (CH), 120.6 (CH), 62.1 (CH_2), 34.1 (Cq), 31.5 (CH_3) ppm; HRMS *m/z* calcd for $C_{38}H_{41}N_8O_2$ [M + H^+] 641.3347; found 641.3368.

Compound 4. A solution of **6**[S2] (0.097 g, 0.56 mmol) in THF (27 mL) was treated with hydroximoyl bromide **11** (0.113 g, 0.26 mmol) under nitrogen atmosphere, then the solution of triethylamine (0.18 mL, 1.30 mmol) in THF (1 mL) was added dropwise over a period of 5 min. The mixture was stirred at reflux for 3 days. After reaction, the volatile solvent was removed under reduced pressure. Subsequently, water (100 mL) was added and the suspension was extracted with CH_2Cl_2 (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford the crude reaction mixture, which was washed with MeOH and collected by filtration to give 85 mg (51% yield) of product **4** as an orange solid. Mp 221-223 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.5 Hz, 4 H), 7.99 (d, *J* = 8.5 Hz, 4 H), 7.35 (d, *J* = 8.8 Hz, 4 H), 6.94 (d, *J* = 8.8 Hz, 4 H), 6.73 (s, 2 H), 5.22 (s, 4 H), 1.31 (s, 18 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.3 (Cq), 161.8 (Cq), 155.5 (Cq), 153.3 (Cq), 144.7 (Cq), 131.4 (Cq), 127.7 (CH), 126.5 (CH), 123.6 (CH), 114.2 (CH), 101.4 (CH), 61.6 (CH_2), 34.2 (Cq), 31.5 (CH_3) ppm; HRMS *m/z* calcd for $C_{40}H_{41}N_4O_4$ [M + H^+] 641.3122; found 641.3121.

***4,4'-Diazidoazobenzene 9*.** 4,4'-Diaminoazobenzene **7**[S3] (1.89 g, 8.90 mmol) was dissolved in water (39 mL) first and then $HCl_{(aq)}$ (100 mL) and $NaNO_2$ (3.07 g, 44.52 mmol) was added slowly at 0 ^oC with stir for 2 hr. After that, $NaNO_2$ (3.07 g, 44.52 mmol) solubilized in water (39 ml) was added dropwise, and then stirred for 1.5 hr. The product was precipitated with some ice, collected by filtration and washed three times with 100 mL cold water and dried under room temperature to give an orange powder **9** (2.11 g, 90 %). R_f = 0.90 (ethyl acetate/*n*-hexane = 2/1); mp 136-138 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 4 H), 7.16 (d, *J* = 8.0 Hz, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7 (Cq), 142.6 (Cq), 124.6 (CH), 119.6 (CH) ppm; EI-MS *m/z* for 264.1 [M^+], 236.1, 208.1.

4,4'-Dioximeazobenzene 10. To a suspension of **8**[S4] in EtOH (103 mL) and H_2O (103 mL) was added hydroxylamine hydrochloride (0.34 g, 4.94 mmol) at 0 °C. Then NaOH (0.40 g, 9.87 mmol) was added with stirring. Then the solution was stirred at room temperature for 1 h, acidified with 1 N $HCl_{(aq)}$ to pH = 7 at 0 °C, and extracted with diethyl ether. The organic layer was dried over $MgSO_4$, and concentrated under vacuum to give product **10** (0.53 g, 96 %). R_f = 0.48 (ethyl acetate/*n*-hexane = 1/1); mp 252-254 °C; ^{1}H NMR (400 MHz, d_6-Acetone): δ = 11.02 (s, 2 H), 8.23 (s, 4 H), 7.96 (d, J = 8.5 Hz, 4 H), 7.83 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, d_6-Acetone): δ = 152.8 (Cq), 147.7 (CH), 136.3 (Cq), 127.5 (CH), 123.1 (CH) ppm; HRMS *m/z* calcd for $C_{14}H_{13}N_4O_2$ [M + H^+] 269.1033; found 269.1037.

4,4'-di(hydroximoyl bromide)azobenzene 11. To a solution of **10** (0.41 g, 1.52 mmol) in DMF (3.04 mL) was added *N*-bromosuccinimide (0.68 g, 3.80 mmol) in small portions while keeping the temperature at 0 °C. The mixture was stirred at 0 °C for 1 h, poured into water, and extracted with dichloromethane (20 mL × 2). The organic layer was washed with brine and dried over $MgSO_4$, and the solvent was removed to give product **11** (0.42 g, 65%). R_f = 0.58 (ethyl acetate/*n*-hexane = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 (d, J = 8.6 Hz, 4 H), 7.69 (d, J = 8.6 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 152.8 (Cq), 133.1 (CH), 123.8 (CH), 116.7 (Cq) ppm.

Table S1. Gelation properties of azobenzene derivatives **1**-**4** in various organic solvents.

Solvent	**1**	**2**	**3**	**4**
CH_2Cl_2	S[a]	S	I	S
$CHCl_3$	S	S	P	S
1,2-dichloroethane	S	P	I	P
DMSO	S	S	G (5.0 w/v%)	P
DMF	S	S	G (5.0 w/v%)	P
THF	S	S	P	S
benzene	P[b]	P	P	P
toluene	S	P	P	P
p-Xylene	G[c] (3.3 w/v%)[d] 48 °C[g]	P	P	P
p-dioxane	S	S	P	S
pyridine	S	S	PG[f]	P
ethyl acetate	S	S	I	P
acetone	S	S	I	PG
acetonitrile	G (1.4 w/v%)[d] 40 °C[g]	P	I	P
n-hexane	I[e]	I	I	I
MeOH	G (0.15 w/v%)[d] 65 °C[g]	I	I	I
EtOH	G (0.16 w/v%)[d] 78 °C[g]	I	I	I
n-propanol	G (0.45 w/v%)[d] 78 °C[g]	P	I	I
Isopropanol	G (0.19 w/v%)[d] 75 °C[g]	I	I	I
n-butanol	G (0.71 w/v%)[d] 70 °C[g]	P	I	P
t-butanol	G (0.53 w/v%)[d] 63 °C[g]	I	I	I

[a] S = solution; [b] P = Precipitate; [c] G = gel; [d] w/v% = the minimum amount of sample (g) which forms gel in 100 mL of solvent; [e] I = Insoluble; [f] PG = Partial gel; [g] Tg = sol-gel transition temperature (°C) at minimum gelation concentration (MGC).

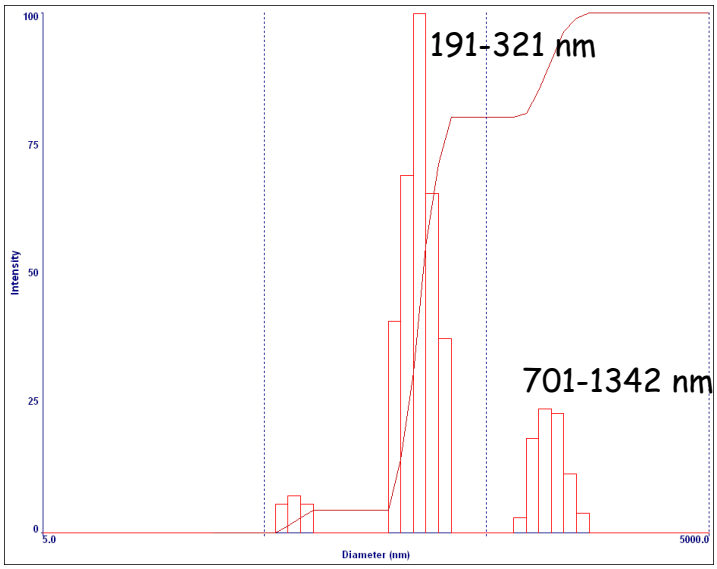


Fig. S1. DLS diagram of a solution of *E*-**1** (1 mM) in acetonitrile at 25 ^{o}C.

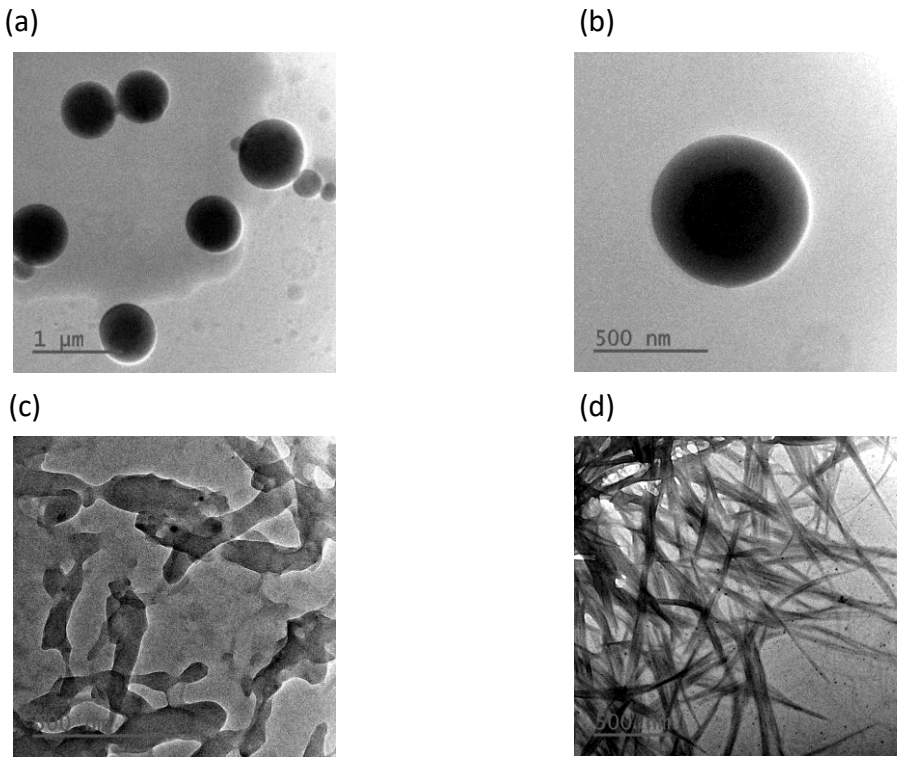


Fig. S2. TEM images of *E*-**1** (1 mM) in (a) and (b) acetonitrile, (c) methanol, and (d) *p*-xylene.

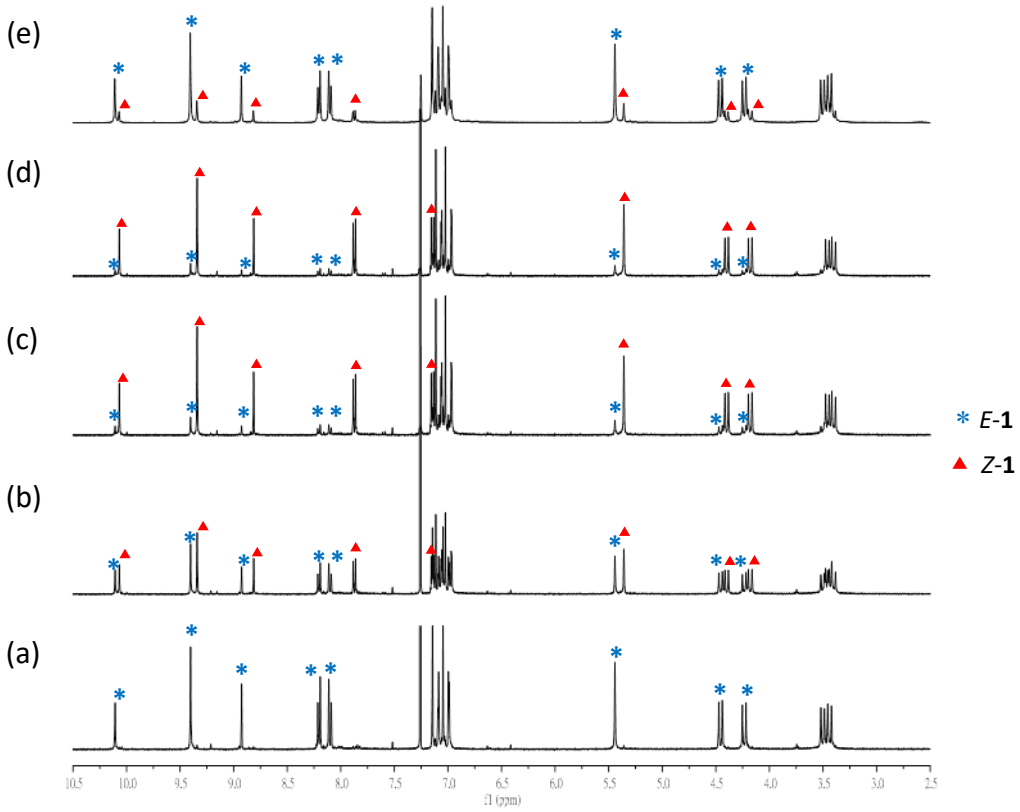


Fig. S3. The ^{1}H NMR spectra of *E*-**1** (1 mM, $CDCl_3$) (a) before and after irradiation of the solution (a) by 365 nm light for (b) 10 min, (c) 20 min, (d) 30 min, and (e) irradiating the sample (d) with a visible light (> 450 nm) for 1 h.

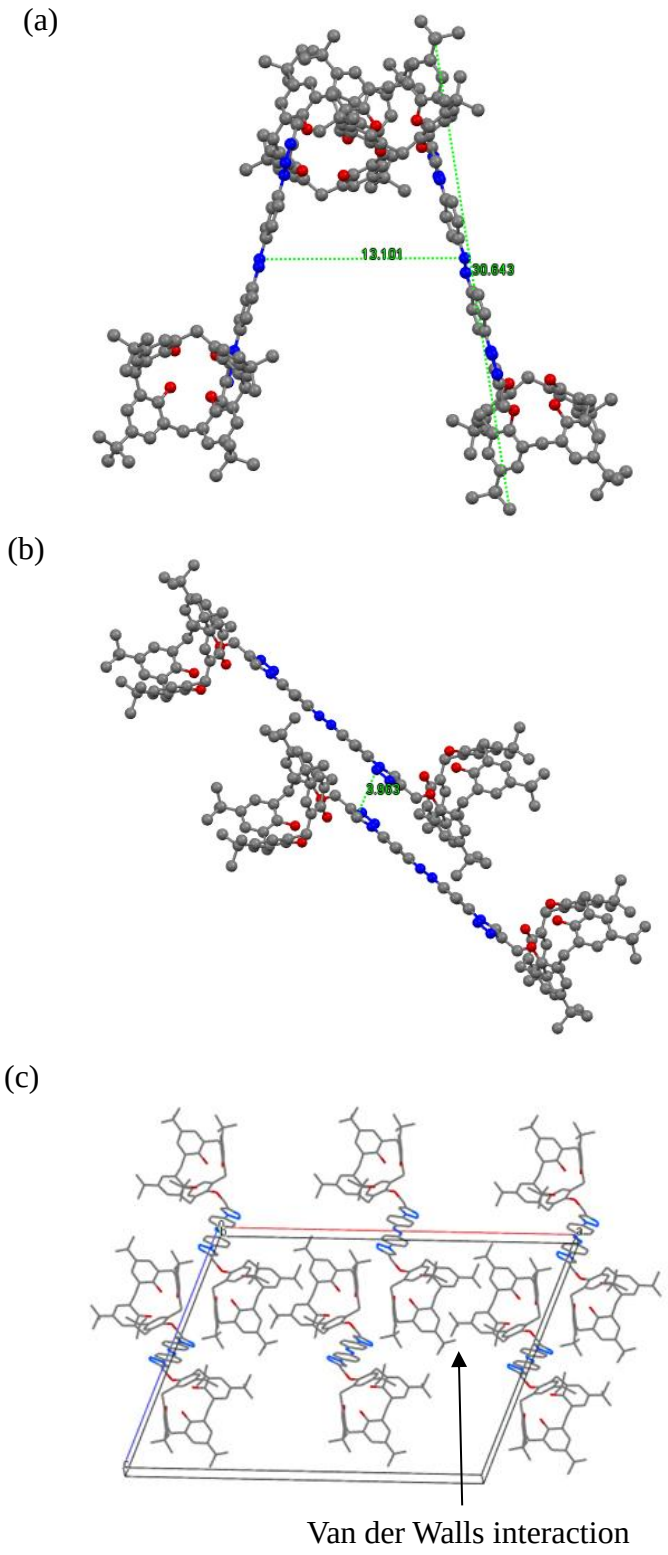


Fig. S4. X-ray single crystal structures of *E*-**1** with (a) the intermolecular distance between the two azo groups of *E*-**1** and its molecular length, (b) the dipolar interactions of two *E*-**1** wiht an interplanar distance of 3.963 Å between the two bistriazolylazobenzene moieties, and (c) evidence of the Van der Walls interaction between the upper-rims of two *E*-**1** molecules.

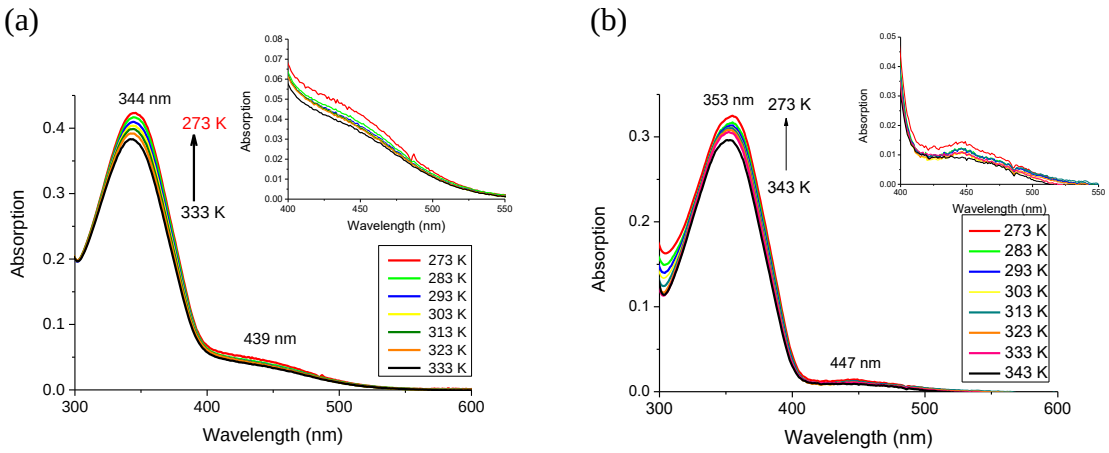


Fig. S5. Variable Temperature (333 → 273 K) UV-Vis spectra of *E*-**1** (10^{-5} M) in (a) acetonitrile and (b) *para*-xylene.

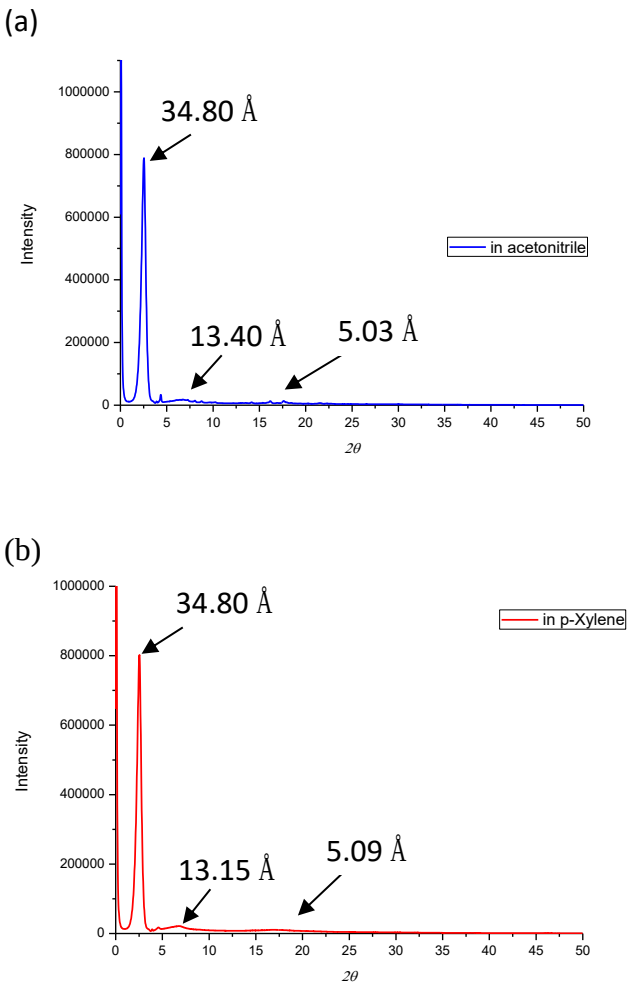


Fig. S6. X-ray powder diffraction (XRD) of *E*-**1** in (a) acetonitrile and (b) *para*-xylene.

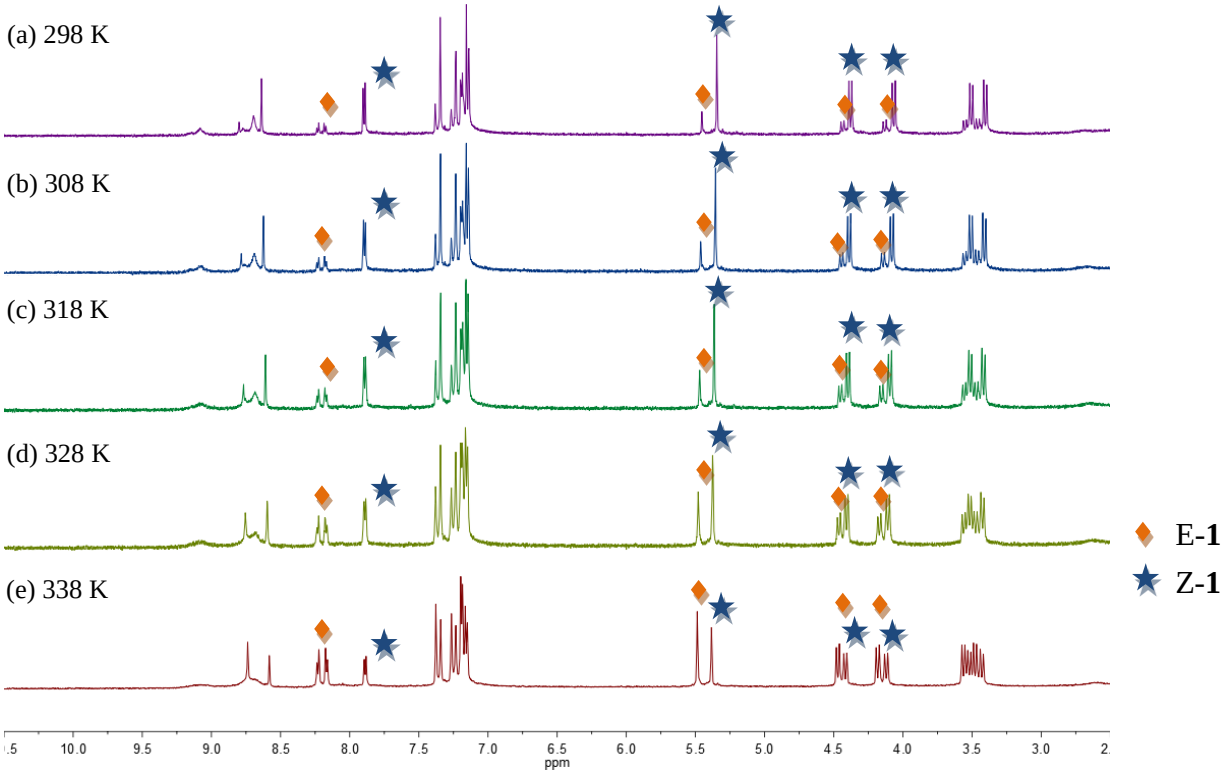


Fig. S7. Variable temperature ^{1}H NMR spectra (298 to 338 K) of a sample of compound **1** (1 mM, CD_3CN) that was irradiated with UV for 20 min and its respective *E*-**1**/*Z*-**1** ratios at different temperatures: (a) 1/4 at 298 K, (b) 1/3 at 308K, (c) 2/5 at 318K, (d) 1/2 at 328K, and (e) 4/3 at 338K.

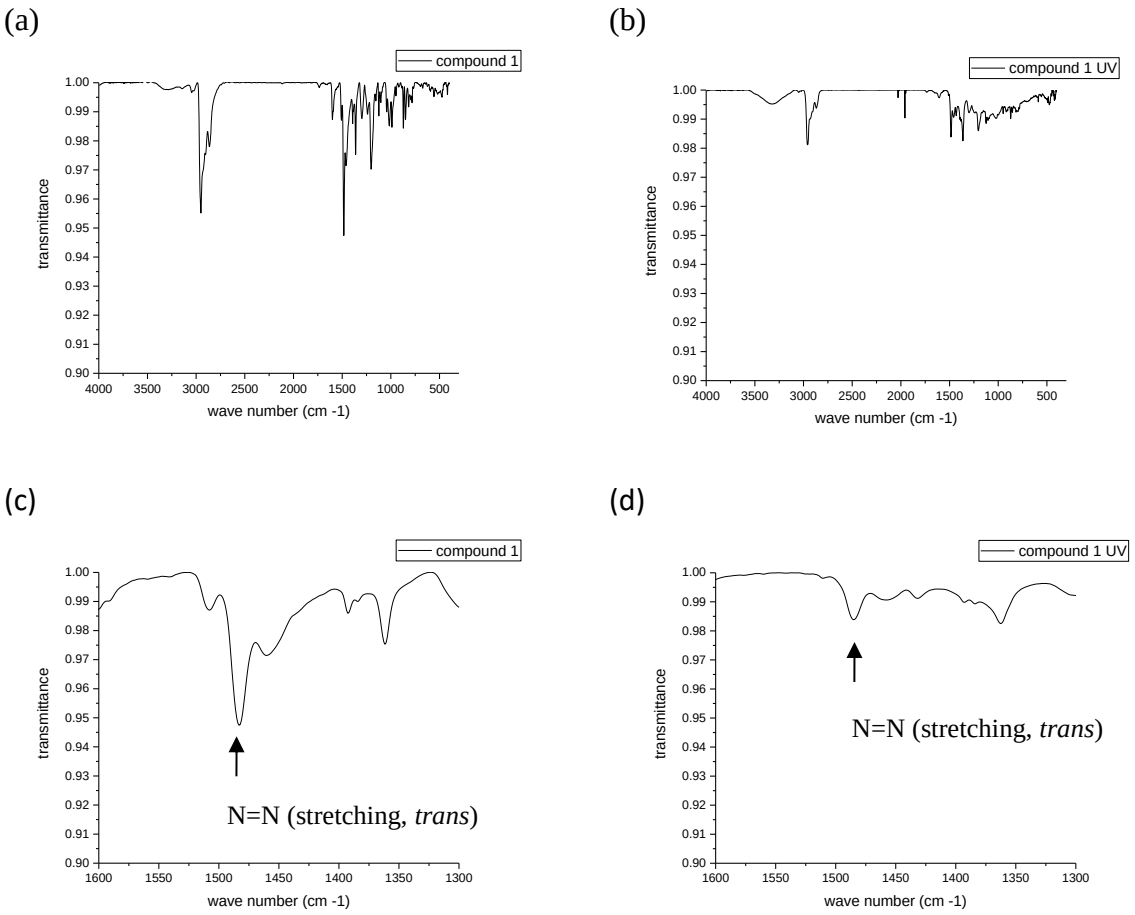


Fig. S8. (a) IR spectrum of compound **1** (1 mM in CH_3CN) and (b) its respective IR spectrum after UV irradiation for 1 h. Spectra (c) and (d) are expanded plots of spectra (a) and (b) which showed that the *trans* N=N stretching at 1480 cm^{-1} decreased by UV irradiation.

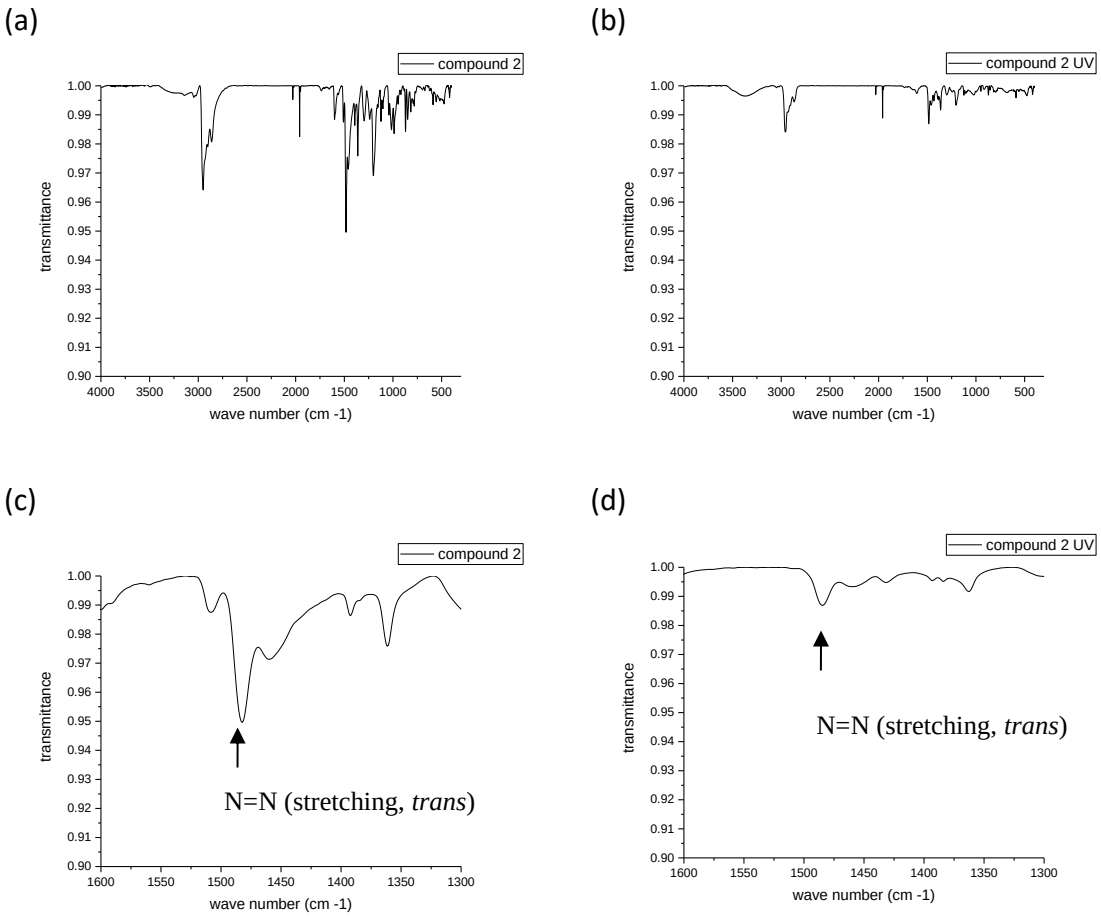


Fig. S9. (a) IR spectrum of compound **2** (1 mM in CH_2Cl_2/MeOH = 1/5) and (b) its respective IR spectrum after UV irradiation for 1 h. Spectra (c) and (d) are expanded plots of spectra (a) and (b) which showed that the *trans* N=N stretching at 1480 cm^{-1} decreased by UV irradiation.

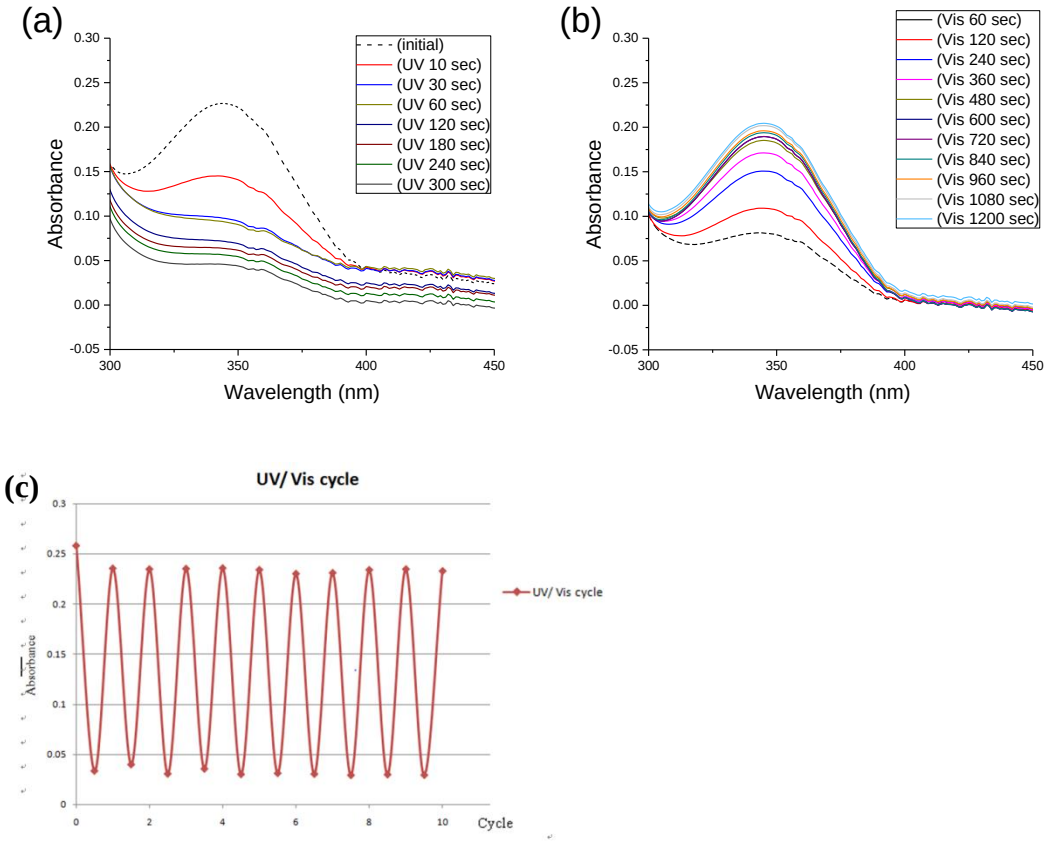


Fig. S10. The UV/Vis spectra of compound **1** (10 μM, CH_3CN) (a) irradiated by UV for different duration, (b) after further irradiation of sample (a) for different duration, and (c) the changes in absorbance of **1** with ten different UV/Vis irradiation cycles. Initially, the absorbance of compound **1** at 345 nm dropped from 0.258 to 0.236, which then stayed almost constant (A = 0.235) for the ten cycles.

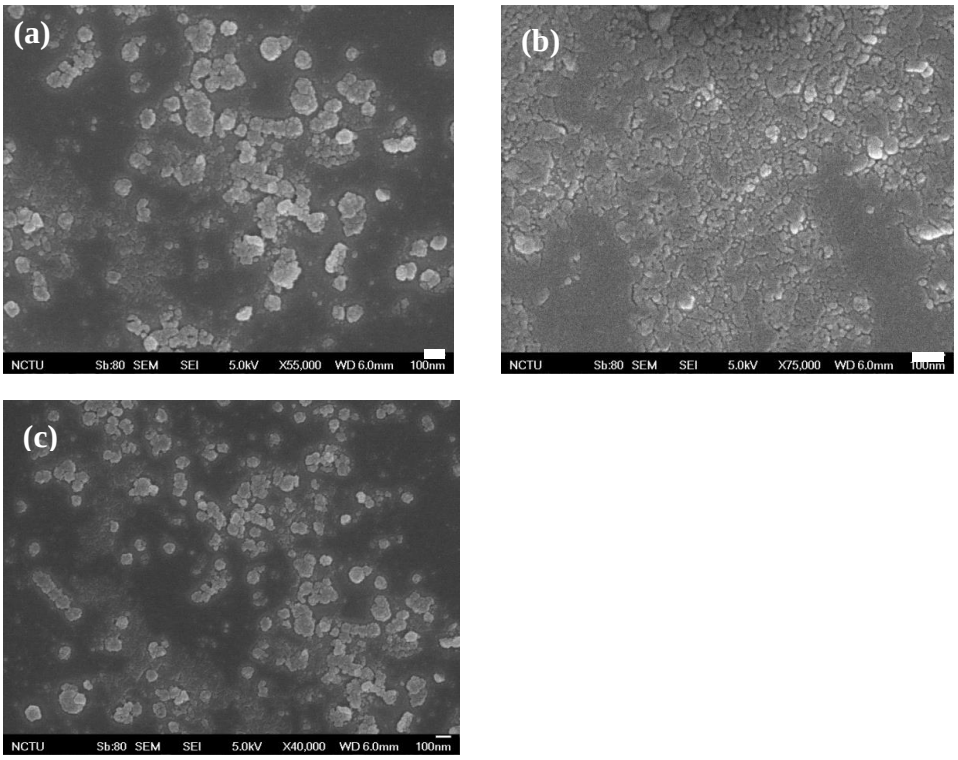


Fig. S11 SEM images of samples of molecule **1** (10^{-3} M, CH_3CN) after UV light (365 nm) irradiation for 30 min. The white bars on the lower right of Figs. (a)–(c) are 100 nm.

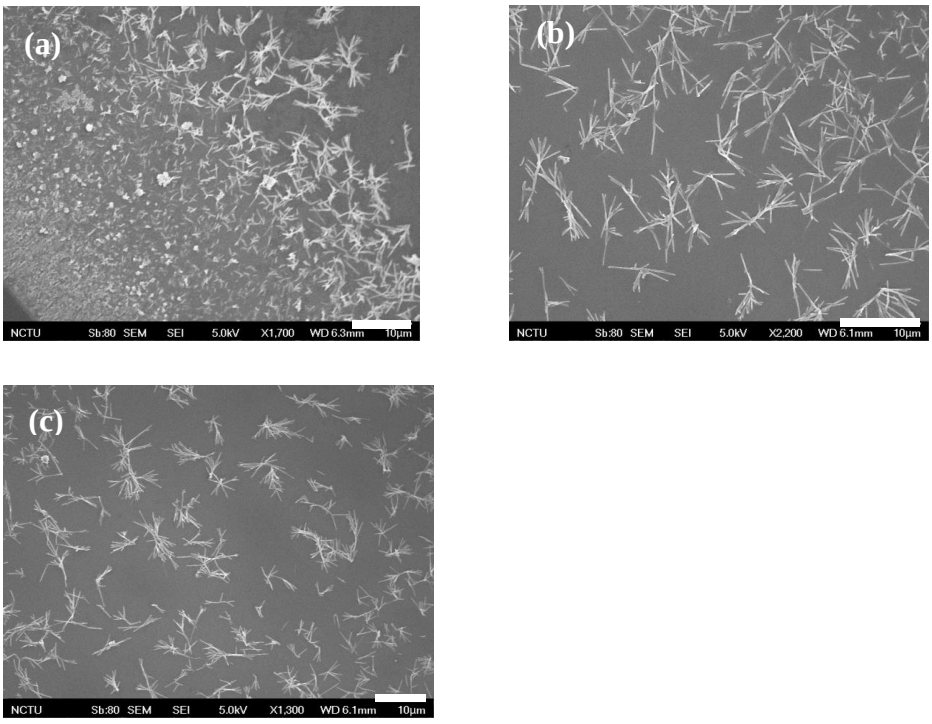


Fig. S12 SEM images of samples of molecule **1** (10^{-4} M, CH_3CN) after UV light (365 nm) irradiation for 30 min. The white bars on the lower right of Figs. (a)–(c) are10 μm.

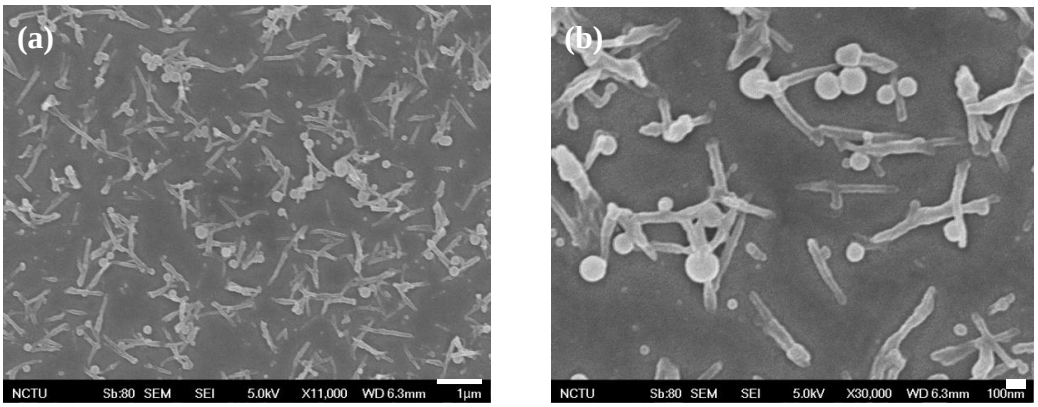


Fig. S13 SEM images of molecule **2** (10^{-3} M, CH_2Cl_2/MeOH (v/v = 1/5)), after UV light (365 nm) irradiation for 30 min. The white bars on the lower right of Figs. (a)–(b) are100 μm.

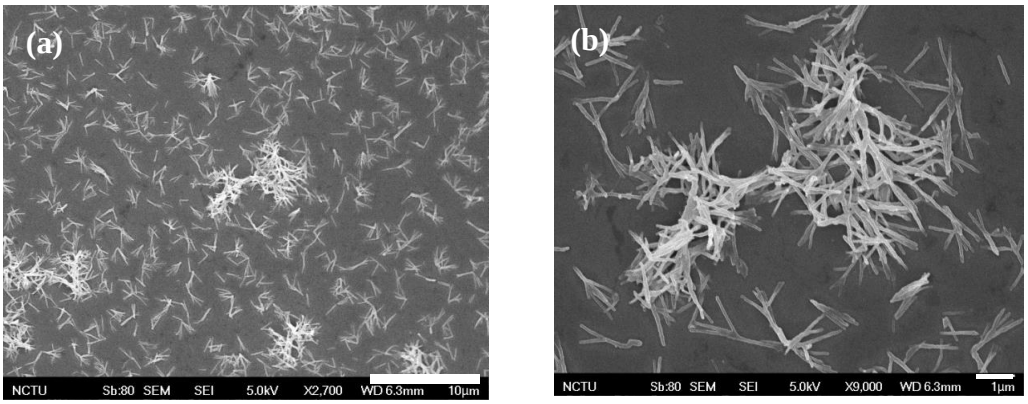


Fig. S14 SEM images of molecule **2** (10^{-4} M, CH_2Cl_2/MeOH (v/v = 1/5)), after UV light (365 nm) irradiation for 30 min. The white bars on the lower right of Fig. (a) was 10 μm and in Figs. (b) was 1 μm.

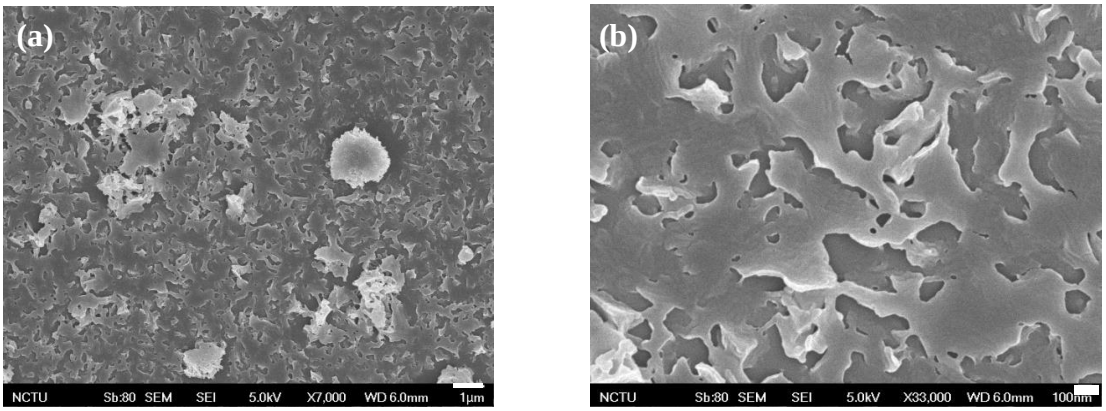


Fig. S15. SEM images of molecule **1** (10^{-3} M, CH_3CN). The white bars on the lower right of Fig. (a) was 1 μm and in Fig. (b) was 100 nm.

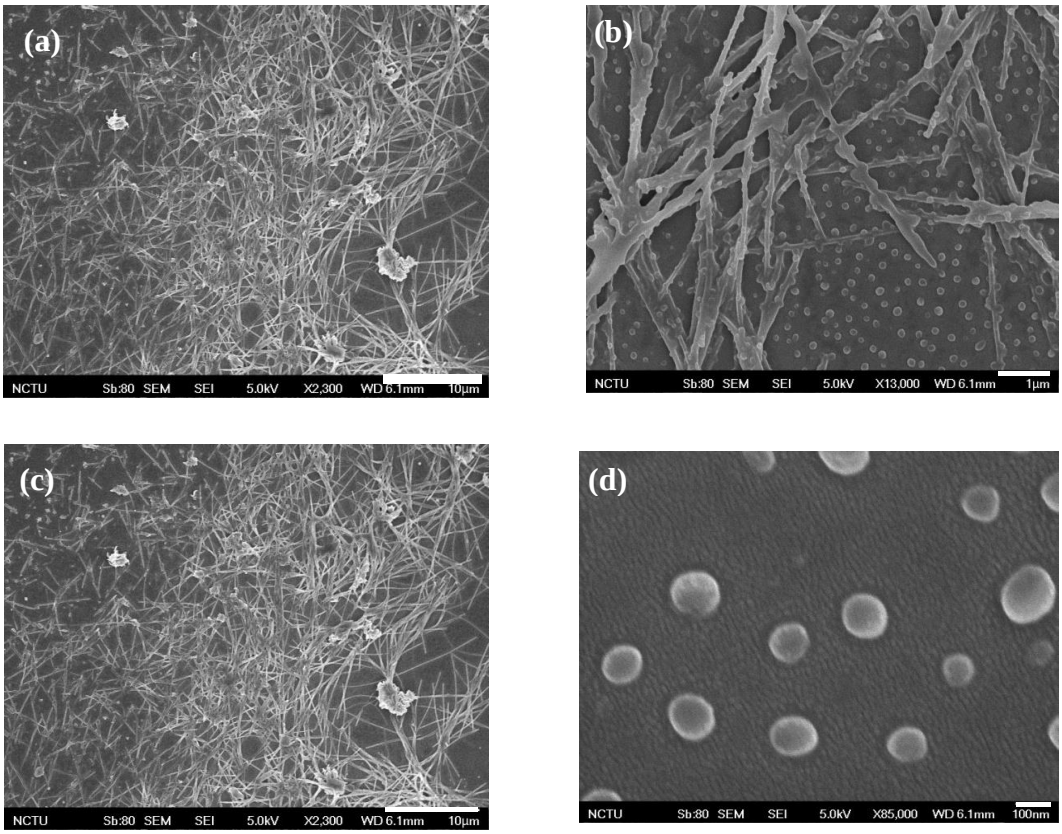


Fig. S16 SEM images of molecule **1** (10^{-4} M, CH_3CN). The white bars on the lower right of Figs. (a) and (c) were 10 μm, Fig. (b) was 1 μm, and Fig. (d) was 100 nm.

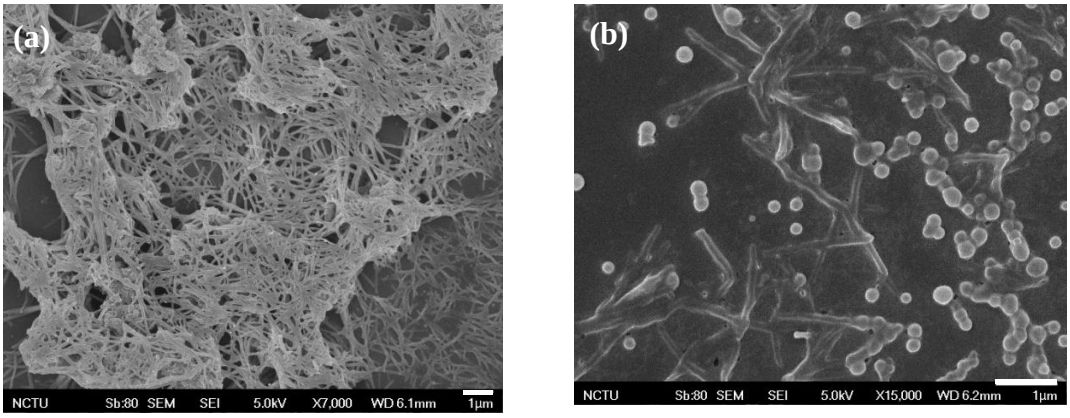


Fig. S17 SEM images of molecule **2** (10^{-3} M in CH_2Cl_2/MeOH (v/v = 1/5)). The white bars on the lower right of Figs. (a) and (b) were 1 μm.

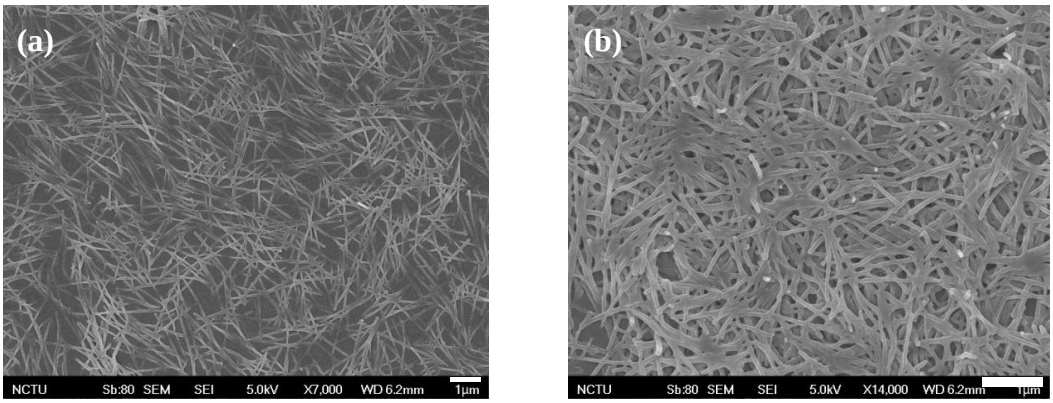


Fig. S18 SEM images of molecule **2** (10^{-4} M in CH_2Cl_2/MeOH (v/v = 1/5)). The white bars on the lower right of Figs. (a) and (b) were 1 μm.

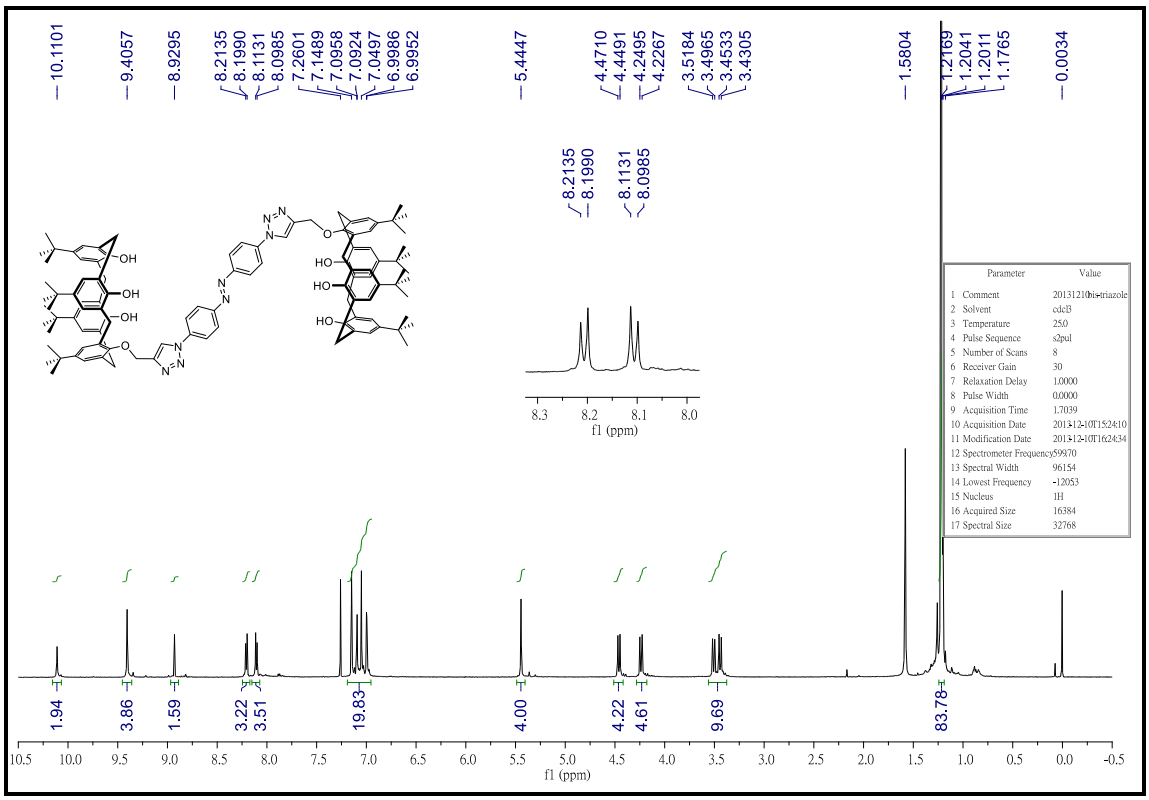


Fig. S19. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *E*-**1**.

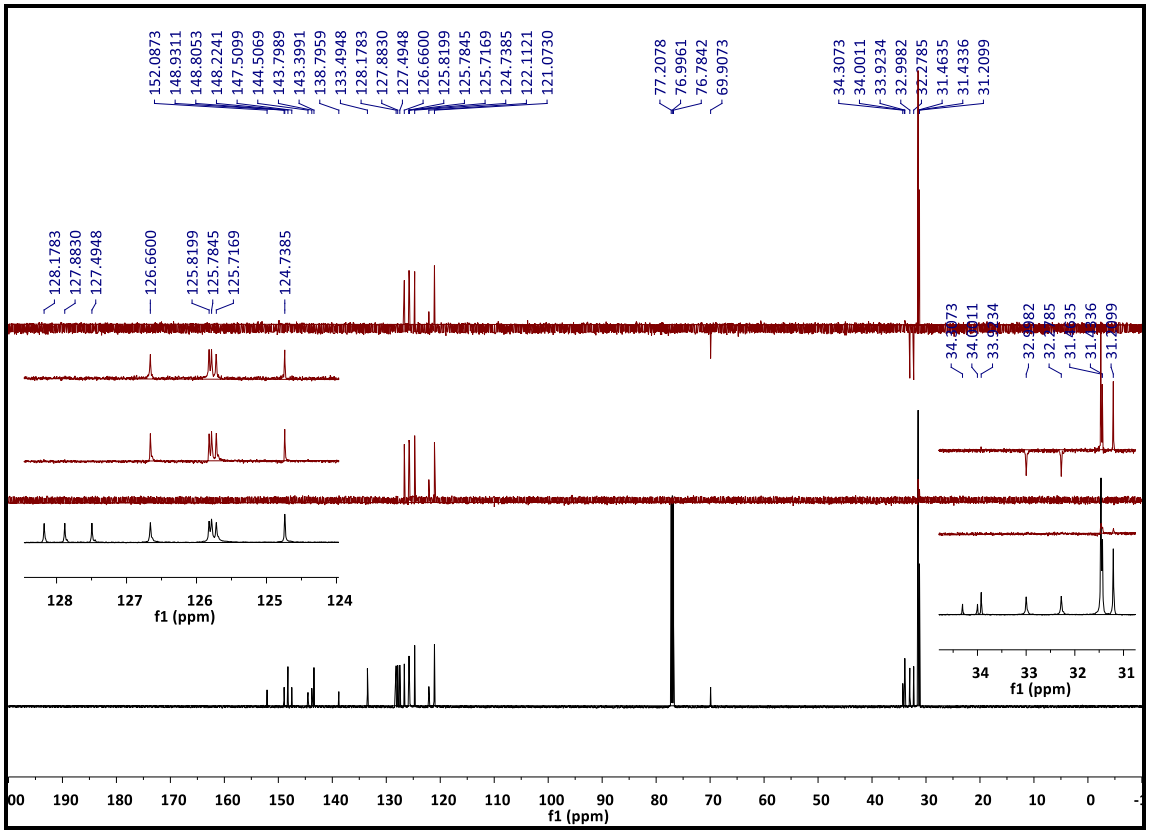


Fig. S20. ^{13}C NMR and DEPT spectra (150 MHz, $CDCl_3$) of *E*-**1**.

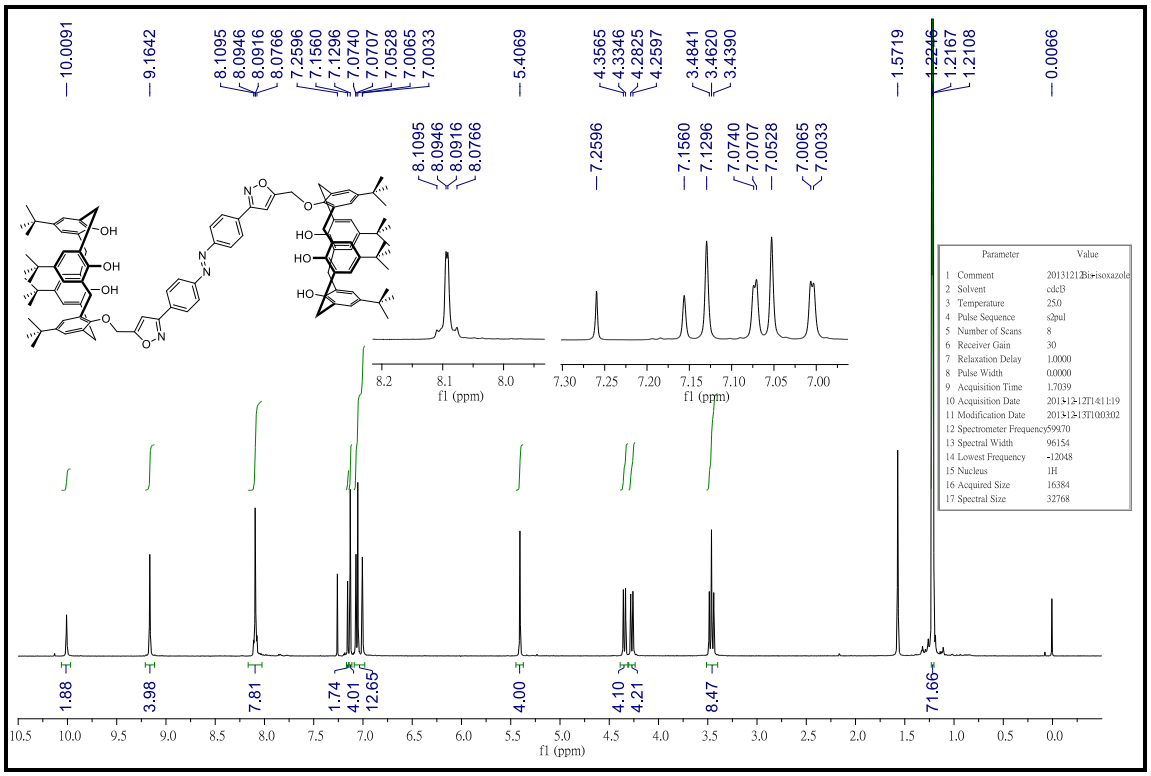


Fig. S21. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of molecule **2**.

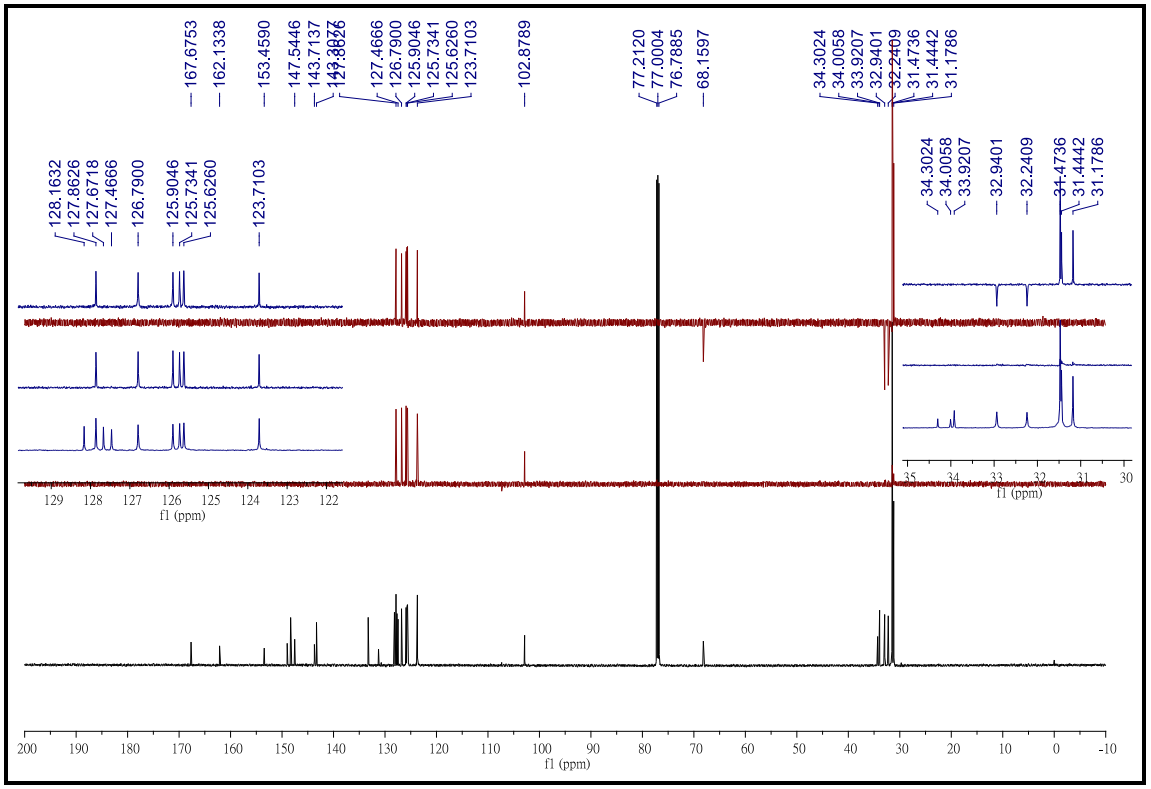


Fig. S22. ^{13}C NMR and DEPT spectra (150 MHz, $CDCl_3$) of molecule **2**.

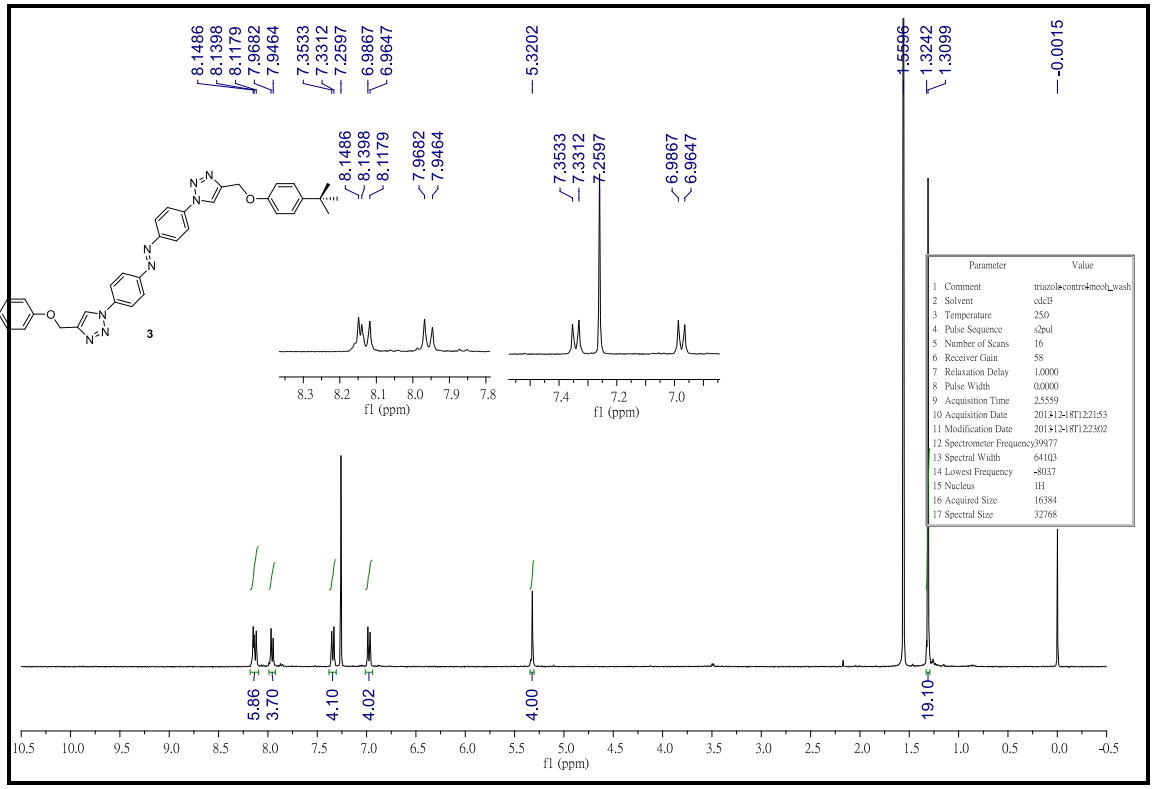


Fig. S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of control molecule **3**.

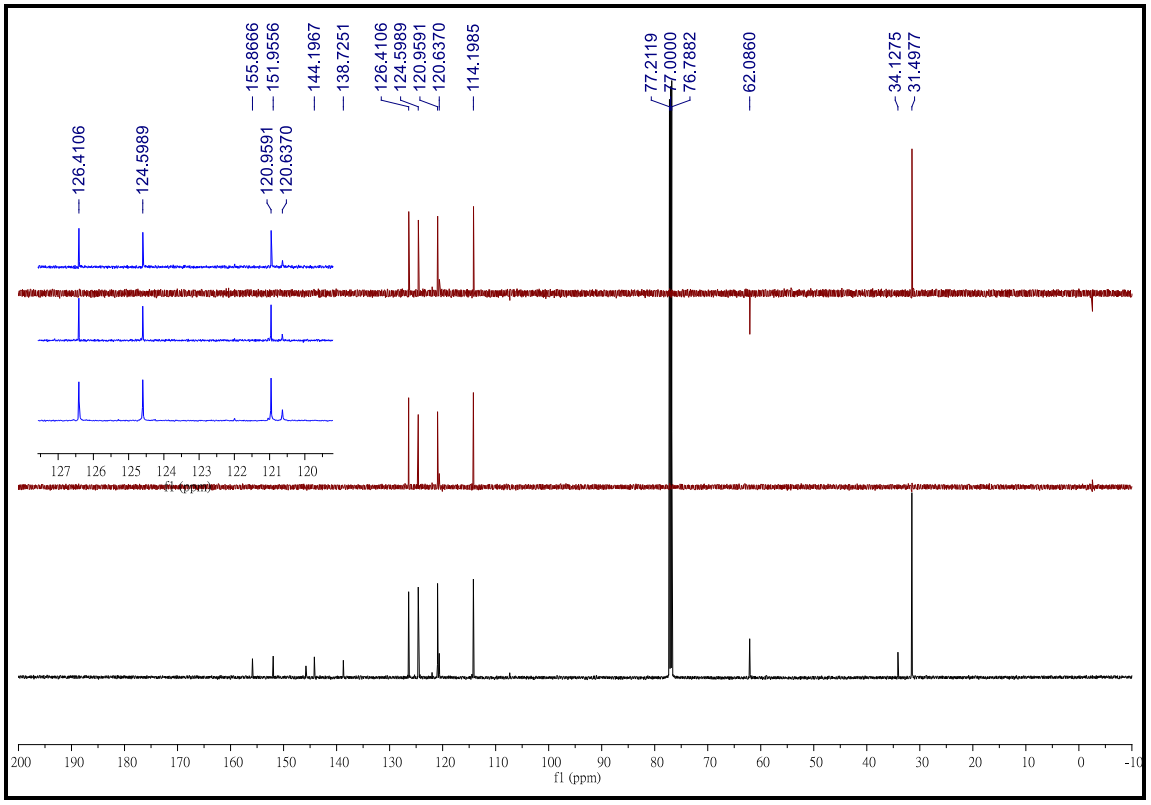


Fig. S24. ^{13}C NMR and DEPT spectra (100 MHz, $CDCl_3$) of control molecule **3**.

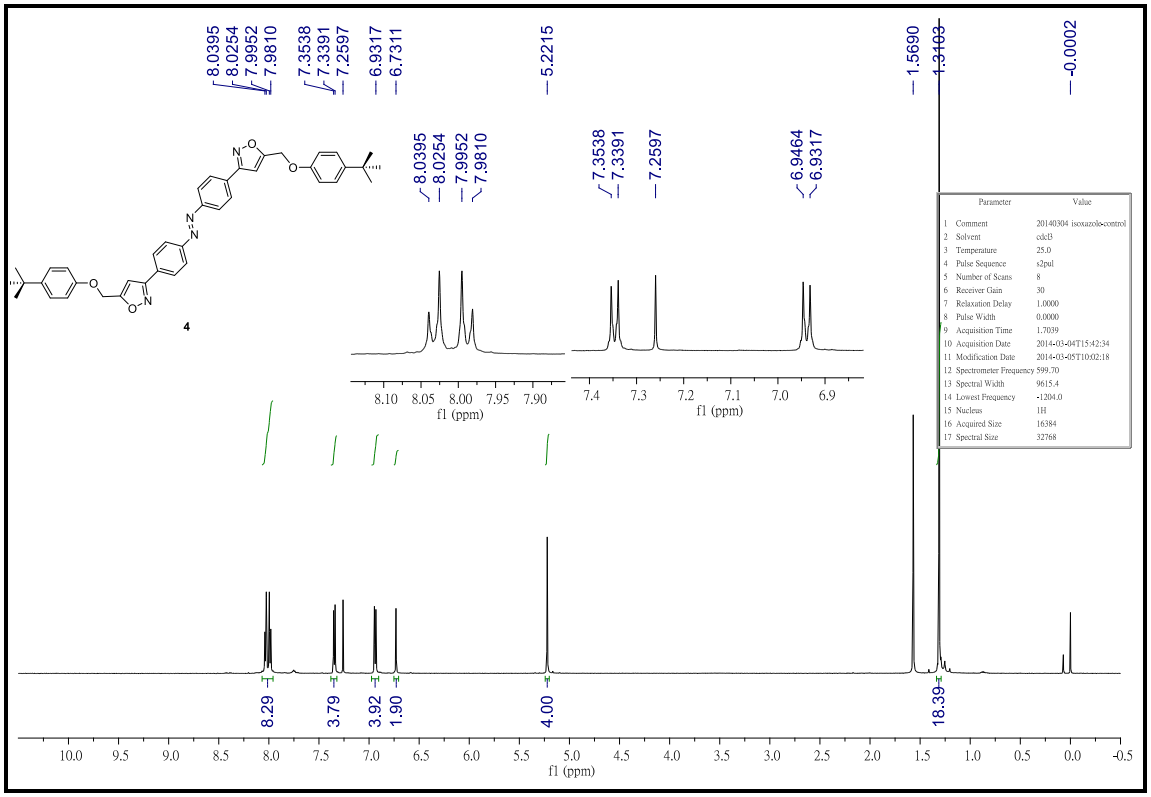


Fig. S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of control molecule **4**.

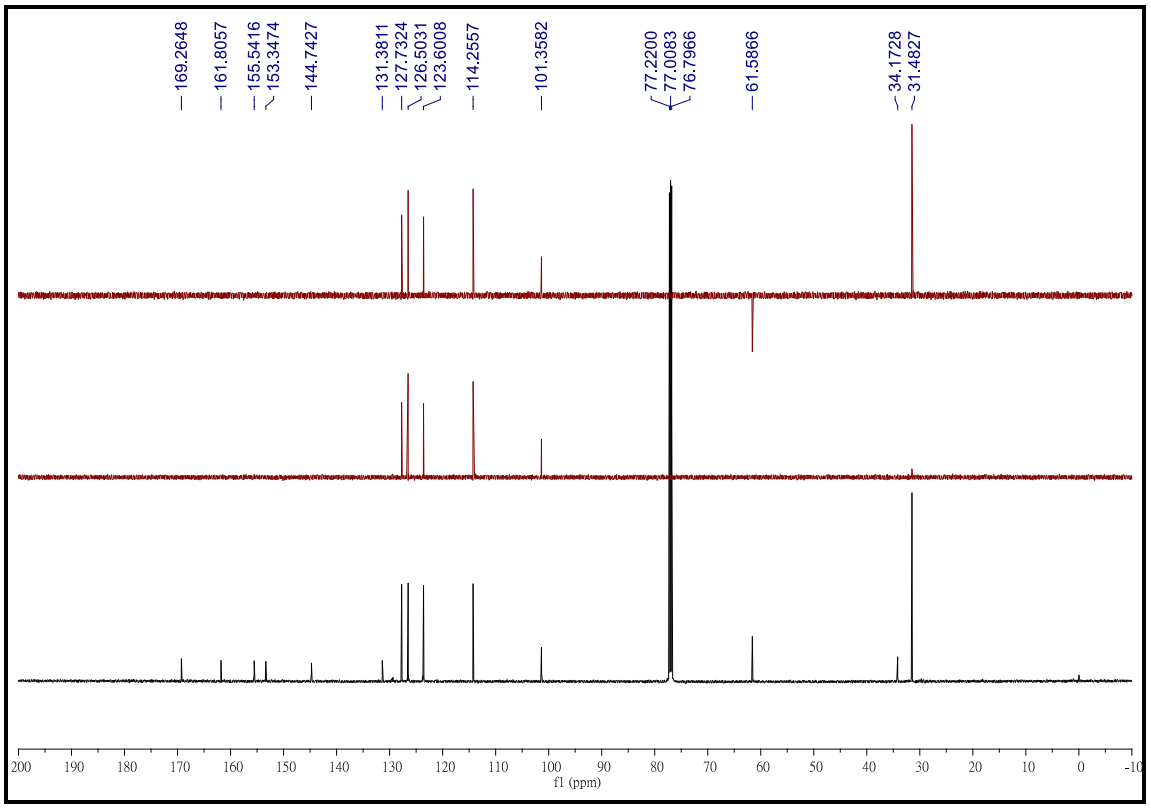


Fig. S26. ^{13}C NMR and DEPT spectra (100 MHz, $CDCl_3$) of control molecule **4**.

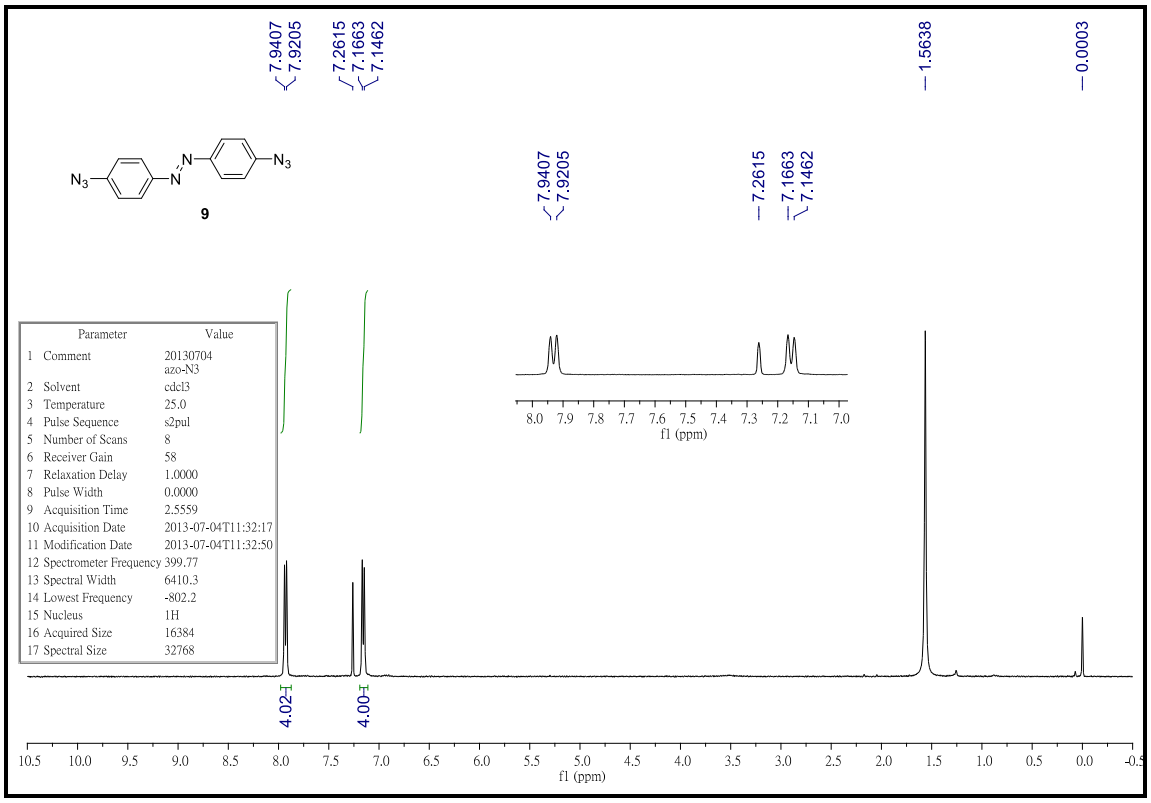


Fig. S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**.

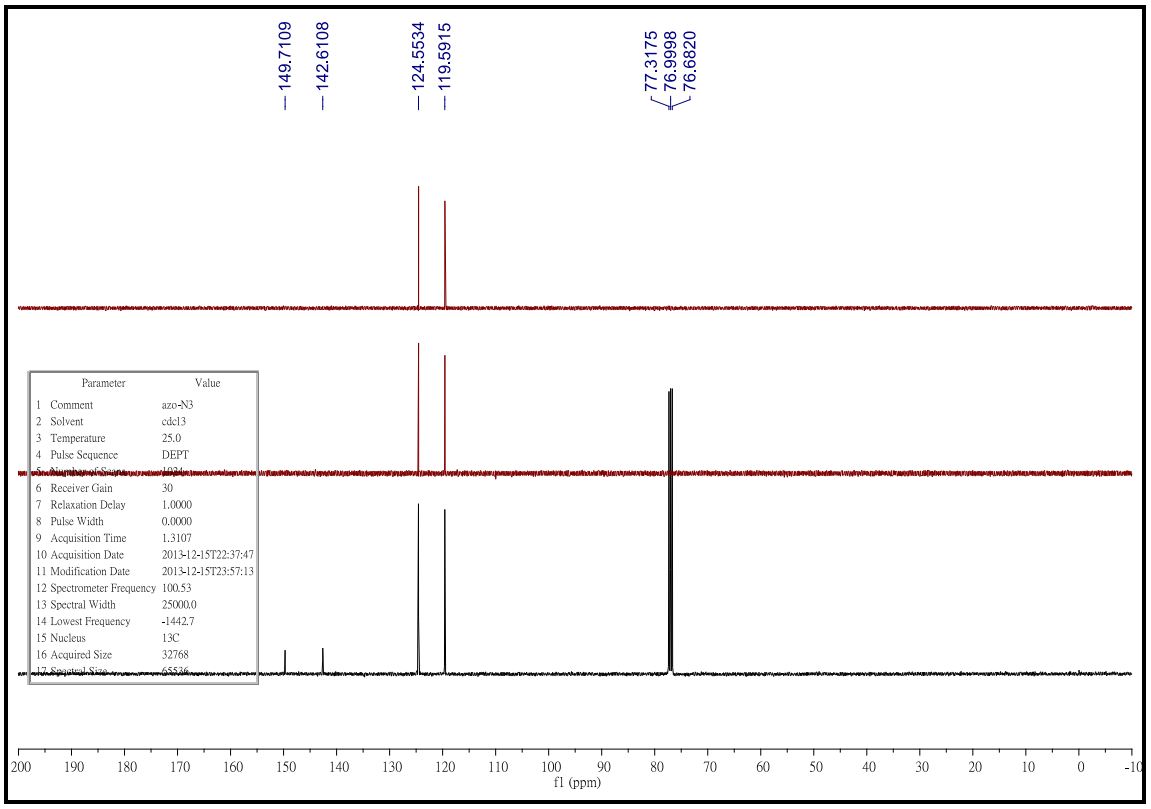


Fig. S28. ^{13}C NMR and DEPT spectra (100 MHz, $CDCl_3$) of of compound **9**.

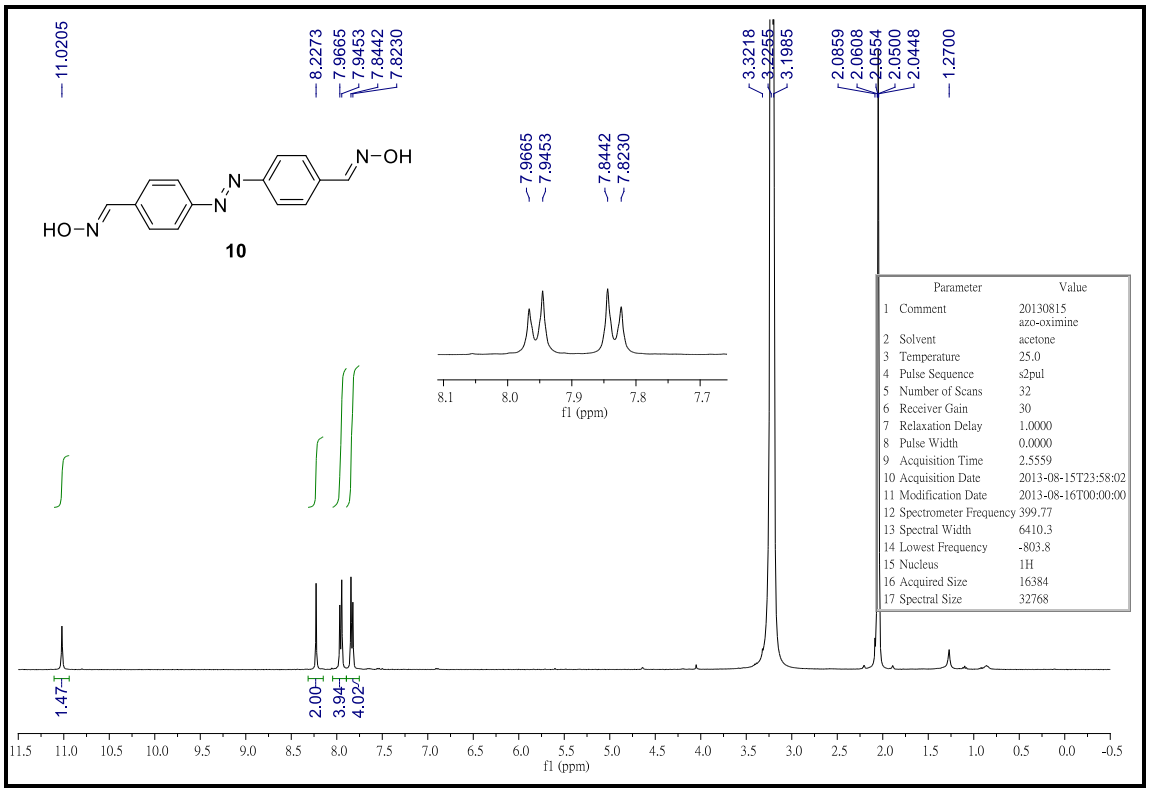


Fig. S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**.

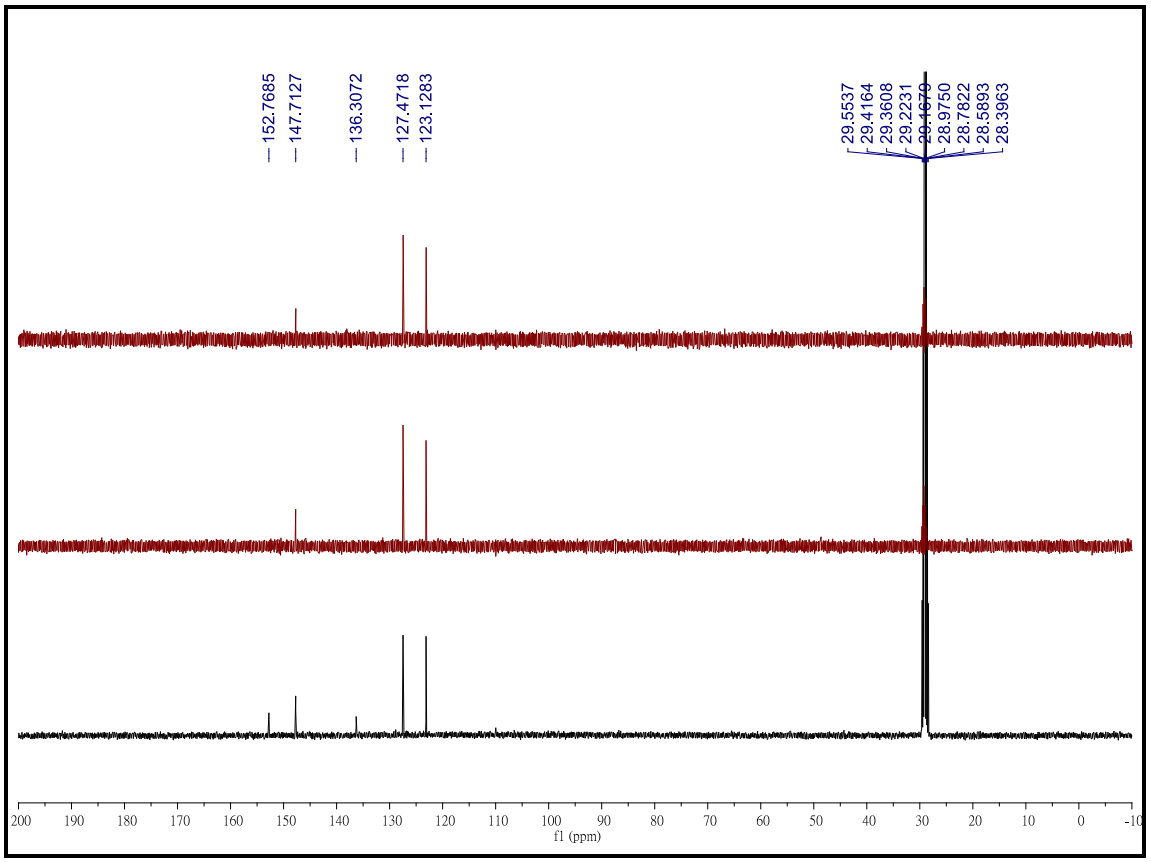


Fig. S30. ^{13}C NMR and DEPT spectra (100 MHz, $CDCl_3$) of of compound **10**.

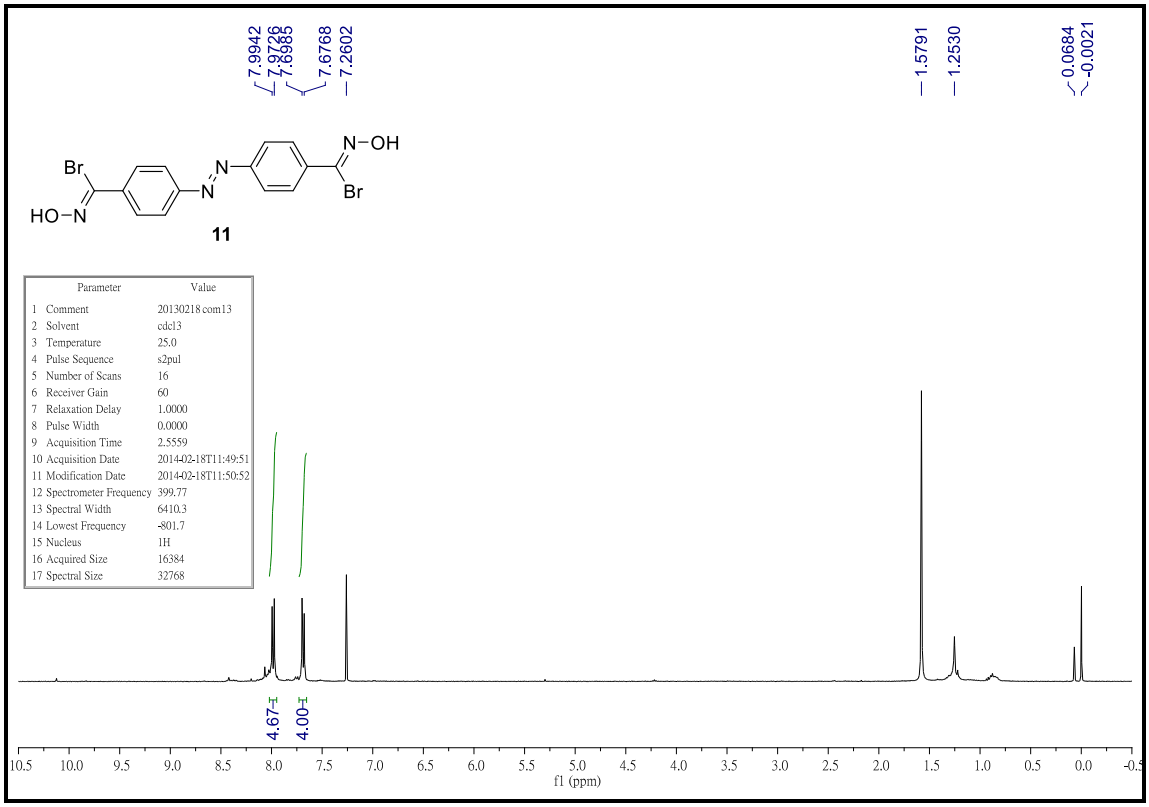


Fig. S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**.

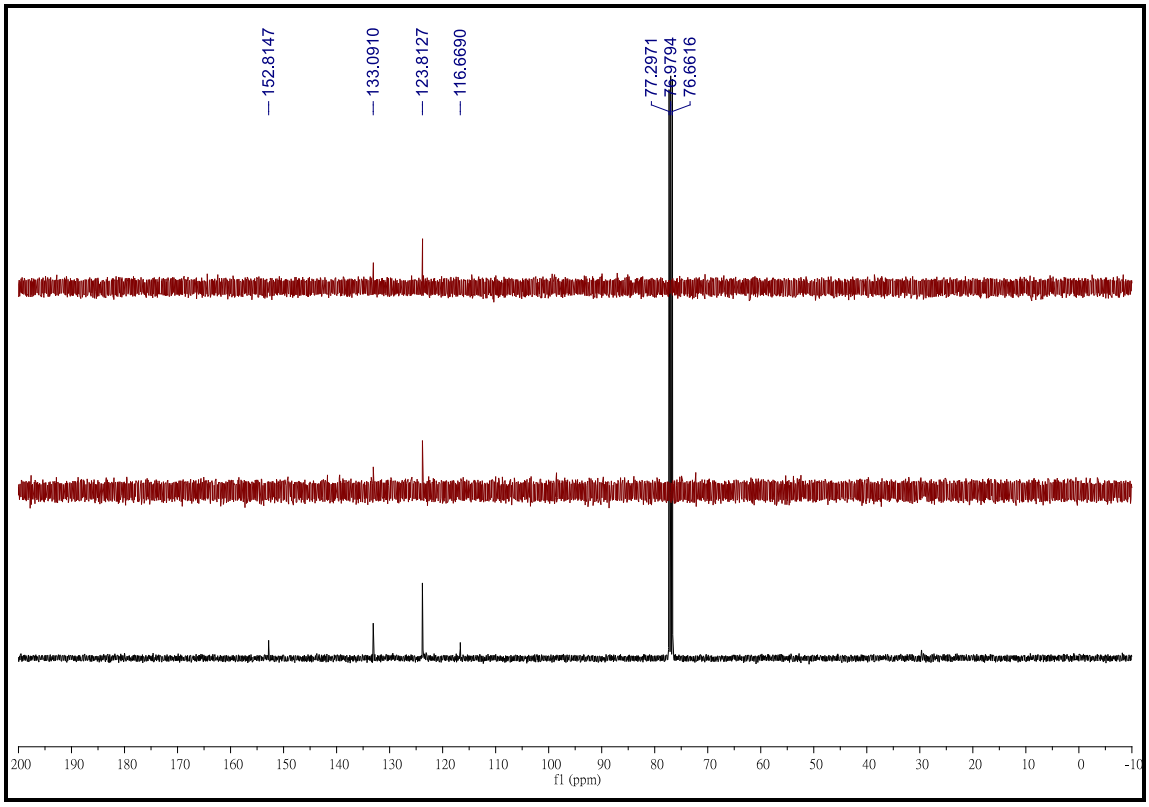


Fig. S32. ^{13}C NMR and DEPT spectra (100 MHz, $CDCl_3$) of of compound **11**.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ic16786_sq

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ic16786_sq

```
Bond precision:  C-C = 0.0047 A          Wavelength=1.54178

Cell:           a=36.5263(18)    b=14.3181(3)       c=26.3568(11)
                alpha=90         beta=110.445(5)    gamma=90
Temperature:    200 K
```

	Calculated	Reported
Volume	12916.0(10)	12916.0(10)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C106 H124 N8 O8 [+ solvent]	?
Sum formula	C106 H124 N8 O8 [+ solvent]	C106 H124 N8 O8
Mr	1638.13	1638.12
Dx,g cm-3	0.842	0.842
Z	4	4
Mu (mm-1)	0.416	0.416
F000	3520.0	3520.0
F000'	3529.69	
h,k,lmax	43,17,31	43,17,31
Nref	11770	11734
Tmin,Tmax	0.905,0.940	0.835,1.000
Tmin'	0.901	

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Correction method= # Reported T Limits: Tmin=0.835 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 67.986

R(reflections)= 0.0719( 8605)     wR2(reflections)= 0.2248( 11734)

S = 1.331                 Npar= 641
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The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
PLAT213_ALERT_2_C Atom C47             has ADP max/min Ratio .....        3.5 prolat
PLAT220_ALERT_2_C Non-Solvent Resd 1   C   Ueq(max)/Ueq(min) Range        4.7 Ratio
PLAT222_ALERT_3_C Non-Solvent Resd 1   H Uiso(max)/Uiso(min) Range        5.3 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C46    --  C48     ..       0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C46    --  C49     ..       0.17 Ang.
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00466 Ang.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
            C106 H124 N8 O8
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......      6.504 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.600         30 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         23 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          8 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          3 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          6 Report
PLAT173_ALERT_4_G The CIF-Embedded .res File Contains DANG Records          1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          2 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1)..        19% Note
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C46'   --  C47'    .       1.71 Ang.
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         91 Note
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed           ! Info
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        53% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          4 Note
PLAT931_ALERT_5_G Found Twin Law ( 0 0  1)[       ] Estimated BASF      0.18 Check
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         17 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  18 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   8 ALERT type 3 Indicator that the structure quality may be low
  12 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT213_ic16786_sq
;
PROBLEM: Atom C47             has ADP max/min Ratio .....        3.5 prolat
RESPONSE: ...
```

```
_vrf_PLAT220_ic16786_sq
;
PROBLEM: Non-Solvent Resd 1    C    Ueq(max)/Ueq(min) Range         4.7 Ratio
RESPONSE: ...
;
_vrf_PLAT222_ic16786_sq
;
PROBLEM: Non-Solvent Resd 1    H Uiso(max)/Uiso(min) Range         5.3 Ratio
RESPONSE: ...
;
_vrf_PLAT234_ic16786_sq
;
PROBLEM: Large Hirshfeld Difference C46     --   C48      ..        0.16 Ang.
RESPONSE: ...
;
_vrf_PLAT340_ic16786_sq
;
PROBLEM: Low Bond Precision on  C-C Bonds ...............     0.00466 Ang.
RESPONSE: ...
;
_vrf_PLAT790_ic16786_sq
;
PROBLEM: Centre of Gravity not Within Unit Cell: Resd.  #           1 Note
RESPONSE: ...
;
_vrf_PLAT906_ic16786_sq
;
PROBLEM: Large K value in the Analysis of Variance ......       6.504 Check
RESPONSE: ...
;
_vrf_PLAT911_ic16786_sq
;
PROBLEM: Missing # FCF Refl Between THmin & STh/L=  0.600          30 Report
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

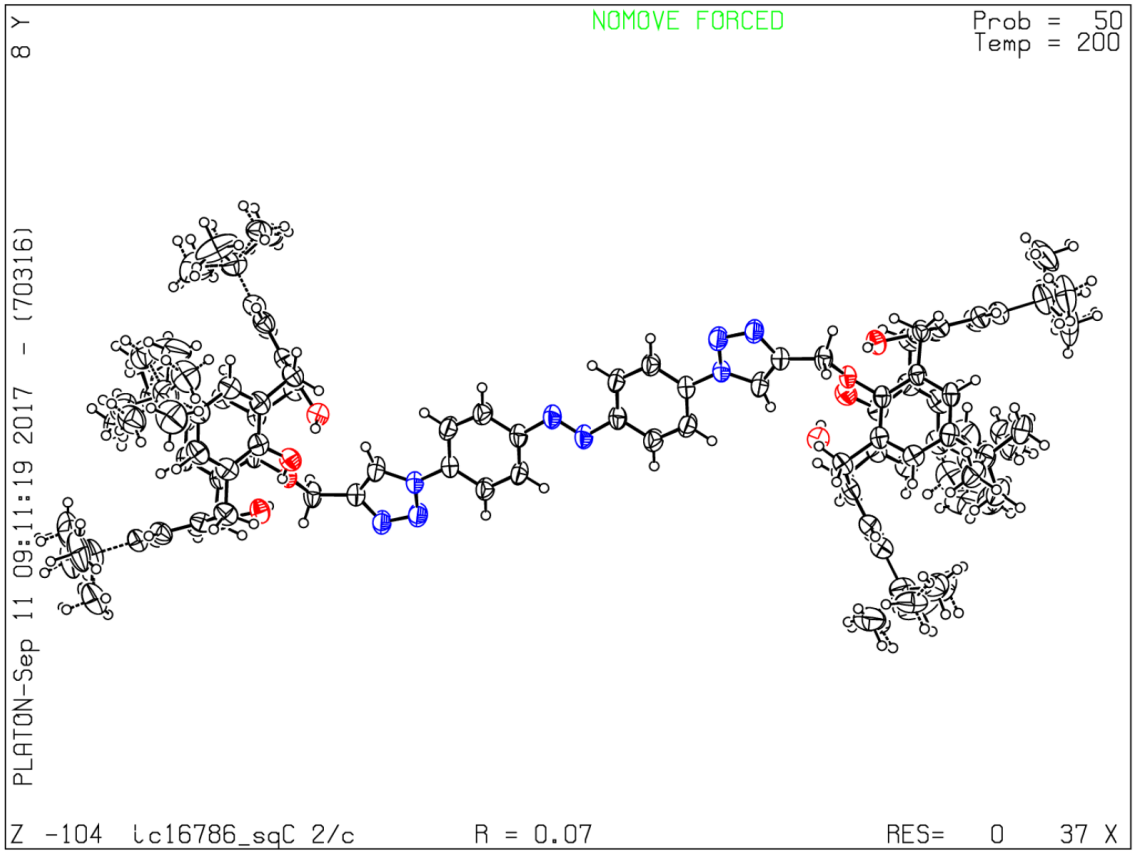
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/08/2017; check.def file version of 27/07/2017

Datablock ic16786_sq - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ic16676

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Bond precision:  C-C = 0.0163 A          Wavelength=0.71073

Cell:            a=36.231(3)     b=14.2891(9)          c=26.170(3)
                 alpha=90        beta=109.636(11)      gamma=90
Temperature:     200 K
```

	Calculated	Reported
Volume	12761(2)	12761(2)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C107.13 H121.38 N4 O10, 4(C H Cl3), 0.874(C H3)	?
Sum formula	C112 H128 Cl12 N4 O10	C112 H128 Cl12 N4 O10
Mr	2115.58	2115.58
Dx,g cm-3	1.101	1.101
Z	4	4
Mu (mm-1)	0.311	0.311
F000	4448.0	4448.0
F000'	4456.66	
h,k,lmax	43,16,31	43,16,31
Nref	11235	18821
Tmin,Tmax	0.946,0.969	0.908,1.000
Tmin'	0.925	

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Correction method= # Reported T Limits: Tmin=0.908 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.675          Theta(max)= 24.999

R(reflections)= 0.1561( 7060)     wR2(reflections)= 0.3969( 18821)

S = 1.784                  Npar= 785
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low ..          38 %
PLAT082_ALERT_2_B High R1 Value ..................................        0.16 Report
PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) ...................        0.40 Report
PLAT340_ALERT_3_B Low Bond Precision on  C-C Bonds ...............     0.01631 Ang.
```

Alert level C

```
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....        2.12 Report
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C28     --  C29      ..         5.2 s.u.
PLAT234_ALERT_4_C Large Hirshfeld Difference N1      --  C1       ..        0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C4      --  C5       ..        0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C5      --  C6       ..        0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C11     --  C12      ..        0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C20     --  C21      ..        0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C27     --  C28      ..        0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C33     --  C34      ..        0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C34     --  C51      ..        0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C39     --  C40      ..        0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C47     --  C48      ..        0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C47     --  C49'     ..        0.17 Ang.
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         C28 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         C31 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         C33 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of          C9 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C29 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C39 Check
PLAT334_ALERT_2_C Small Average Benzene  C-C Dist. C25    -C30          1.37 Ang.
PLAT413_ALERT_2_C Short Inter XH3 .. XHn     H21A    ..  H46F     ..        2.12 Ang.
PLAT414_ALERT_2_C Short Intra D-H..H-X       H4      ..  H24A     ..        1.96 Ang.
PLAT416_ALERT_2_C Short Intra D-H..H-D       H3      ..  H4       ..        1.93 Ang.
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of .          48 Ang3
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #           1 Note
              C107.13 H121.38 N4 O10
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          10 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          39 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............           1 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          7 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          3 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1)..        14% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2)..       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3)..       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4)..       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5)..       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  6)..       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms ( 242.50) in Resd. #          1 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   2.63) in Resd. #          2 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   3.45) in Resd. #          3 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   2.37) in Resd. #          4 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   1.55) in Resd. #          5 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   1.75) in Resd. #          6 Check
PLAT395_ALERT_2_G Deviating  X-O-Y  Angle from 120 Deg for  O1          107.6 Degree
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PLAT432_ALERT_2_G Short Inter X...Y Contact  C20    ..  C46'    ..       2.55 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact  C21    ..  C46'    ..       2.95 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact  C43    ..  C46'    ..       1.81 Ang.
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C43    --  C46'    .       1.81 Ang.
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        434 Note
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
```

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  0 ALERT level A = Most likely a serious problem - resolve or explain
  4 ALERT level B = A potentially serious problem, consider carefully
 25 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 25 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 21 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
 27 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/08/2017; check.def file version of 27/07/2017

Datablock ic16676 - ellipsoid plot