Electronic Supplementary Information for

Strong Fluorescence Emission Induced by Supramolecular Assembly and Gelation: Luminescent Organogel from Nonemissive Oxadiazole-Based Benzene-1,3,5-tricarboxamide Gelator

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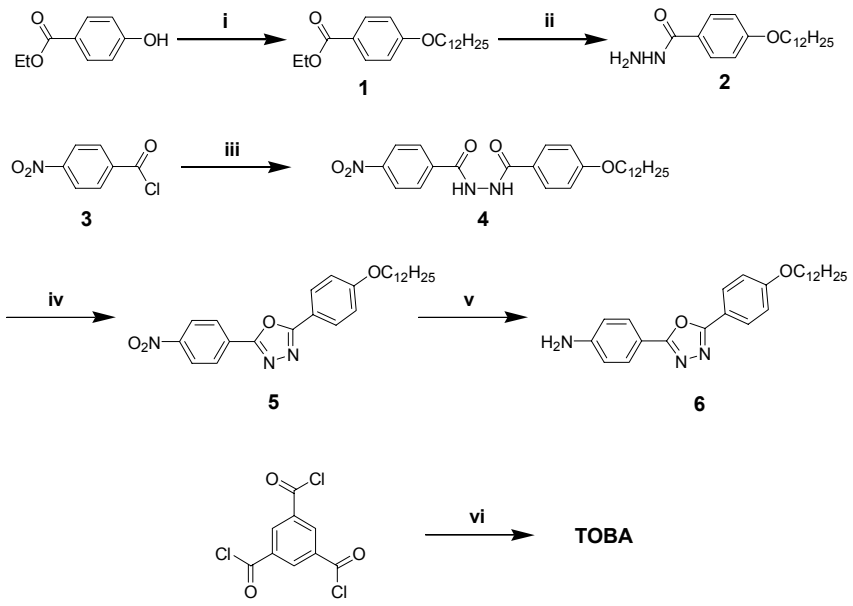
1. Synthesis



i=$BrC_{12}H_{25}$/KOH/EtOH/reflux, **ii**=NH_2NH_2/PTSA/EtOH/reflux, **iii**=TEA/compoud **2**/THF
iv=DMF/$POCl_3$/reflux, **v**=H_2/palladium on activated carbon/THF, **vi**=compound **6**/THF/reflux

4-Dodecyloxybenzoic acid ethyl ester (1). A solution of ethyl 4-hydroxybenzoate **(**10 g, 0.06 mol) and KOH (0.072 mol) in ethanol (100 mL) was stirred at 60 ^{o}C for 30 min and 1-bromododecane (0.12 mol) was slowly added. After refluxing overnight. solvent was evaporated under reduced pressure, and then the product

was washed with water and neutralized with 1 N HCl. The product was extracted with ethyl acetate and dried over $MgSO_4$. The crude product after solvent evaporation was purified by column chromatography on silica gel with ethyl acetate/*n*-hexane (vol. ratio 1/5) as the eluent to obtain 11.8 g of white solid (70% yield).

4-Dodecyloxybenzoic acid hydrazide (2). To a solution of compound **1** (8.45 g, 0.025 mol) and $NH_2NH_2 \cdot H_2O$ (10 ml) in 150 mL of ethanol was added a catalytic amount of *p*-toluenesulfonic acid monohydrate at 60 ^oC. The reaction mixture was heated to 100 ^oC and stirred for 48 h. After the reaction was completed, the mixture was poured into excess water and the collected precipitate was recrystallized from ethanol to give 6.25 g of white solid (74 % yield). ^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.69 (d, 2H), 6.92 (d, 2H), 3.99 (t, 2H).

4-Nitrobenzoyl chloride (3). To a suspension of 4-nitrobenzoic acid **(**2 g, 12 mmol) in $SOCl_2$ (8 mL) was added a catalytic amount of DMF and the mixture was refluxed for 5 h. The evaporation of $SOCl_2$ under reduced pressure gave yellow solid. This crude product was used for the next step without further purification.

4-Nitrobenxoic acid *N'*-(4-dodecyloxybenzoyl)hydrazide (4). Compound **2** (4.6 g, 14.4 mmol) and triethylamine (6.2 mL) were dissolved in 20 mL of THF. To this solution, compound **3** dissolved in 5mL of THF was added dropwise at room temperature. After stirring for 3 h, the mixture was poured into excess water, and the product was extracted with ethyl acetate. The collected organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The yellowish product was used for the next step without further purification (4.7 g, 84% yield). ^{1}H-NMR ($CDCl_3$, 300MHz) δ 8.31 (d, 2H), 8.12 (d, 2H), 7.72 (d, 2H), 6.92 (d, 2H), 3.99 (t, 2H), 0.88 (t, 3H).

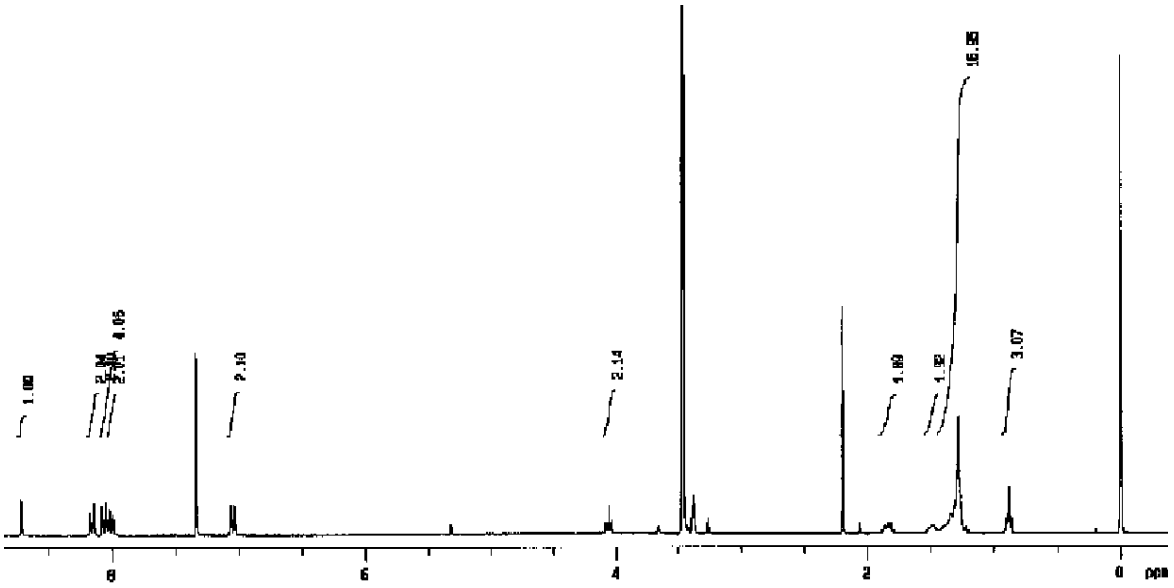
2-(4-Dodecyloxyphenyl)-5-(4-nitrophenyl)-[1,3,4]oxadiazole (5). A suspension of compound **4** (4.5 g, 9.6 mmol) in $POCl_3$ (10 mL) was refluxed for 4 h. After cooling down to room temperature, the resulting solution was poured into ice water and neutralized with 1 N NaOH solution. The collected precipitate was purified by column chromatography on silica gel with dichloromethane/*n*-hexane (vol. ratio 2/1) to yield 3 g of yellowish solid (70% yield). ^{1}H-NMR ($CDCl_3$, 300MHz) δ 8.41 (d, 2H), 8.32 (d, 2H), 8.08 (d, 2H), 7.04 (d, 2H), 4.05 (t, 2H), 0.88 (t, 3H).

4-[5-(4-Dodecyloxyphenyl)-[1,3,4]oxadiazol-2-yl]phenylamine (6). To a solution of compound **5 (**3 g, 7.1 mmol) in THF (50 mL) was added 0.1 g of palladium on activated carbon (5% PD). After the reaction vessel was fully charged with H_2 gas, the mixture was vigorously stirred at room temperature for 12 h. The insoluble part was removed by filtration and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using THFe/*n*-hexane (vol. ratio 1/3) to yield 2.1 g of yellowish solid (75% yield). ^{1}H-NMR ($CDCl_3$, 300MHz) δ 8.03 (d, 2H), 7.92 (d, 2H), 7.04 (d, 2H), 6.76 (d, 2H), 4.02 (t, 2H), 0.88 (t, 3H).

Benzene-1,3,5-tricarboxylic acid tris-({4-[5-(4-dodecyloxyphenyl)-[1,3,4]oxadiazol-2-yl]phenyl}-amide) (TOBA). To a solution of compound **6** (0.34 g, 0.81 mmol) in 20 mL of THF, 1,3,5-benzene-tricarbonyl

trichloride (0.06 g, 0.226 mmol) dissolved in 5mL of THF was added dropwise at room temperature. The mixture was refluxed for 2 h until the liberation of HCl gas was completed. On cooling, gelation occurred to make the whole reaction mixture immobile gel. Soluble parts and solvent were removed by filtration and the filtered xerogel was purified by repeated precipitation from hot chloroform solution into methanol and further washed with hot dichloromethane using Soxhlet apparatus for 1 day, to give 0.23 g of pale yellowish solid (72% yield). Mp 250 ^{o}C; ^{1}H-NMR ($CDCl_3$:methanol-d_4=9:1, 300MHz) δ 8.71 (s, 3H), 8.14 (d, 6H), 8.03 (q, 12H), 7.05 (d, 6H), 4.06 (t, 6H); IR (KBr pellet, cm^{-1}) 3276 (N-H), 1654 (C=O); Elem. Anal. Calcd for C87H105N9O9: C 73.54, H 7.45, N 8.87. Found: C 72.42, H 7.64, N 8.31; MALDI-TOF-MS (Reflector, Positive) 1420.1 (calcd. 1419.8).

^{1}H NMR for the monomer-state TOBA in $CDCl_3$/methanol-d_4 (=9/1 by volume)



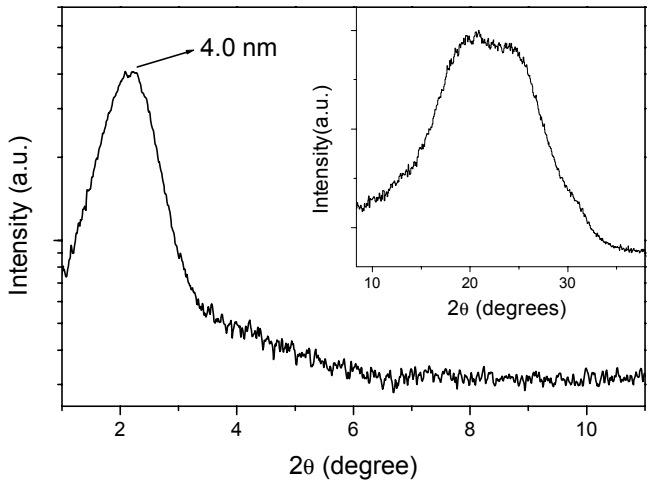
(Signals appearing in the region of 2~6 ppm are inherent peaks from the solvent used.)

2. Experiments for picosecond time-resolved fluorescence kinetic study

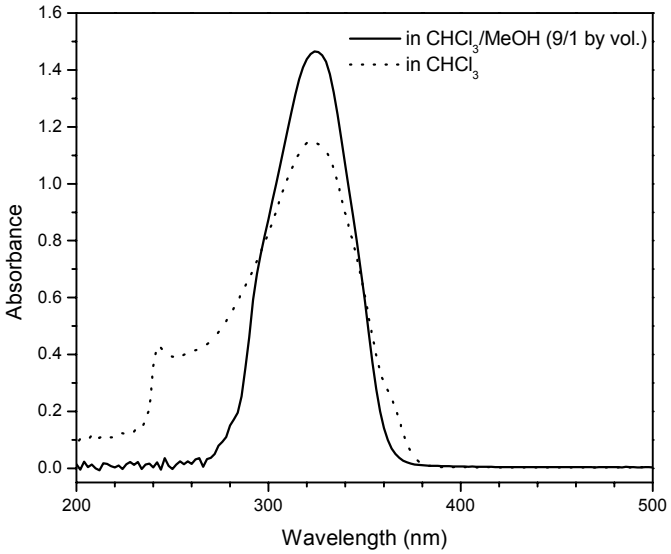
Fluorescence kinetic profiles were obtained by using a mode-locked Nd:YAG laser (Quantel, YG701) and a 10-ps streak camera (Hamamatsu, C2830). Samples were excited at the red edges of absorption bands to discard the short-lived upper-excited fluorescence (S_n-S_1). For edge excitation was used the 386-nm pulses generated through a Raman shifter, filled with methane and pumped by 266-nm laser pulses having the duration of 25 ps. Fluorescence kinetic constants were extracted by fitting profiles measured to computer-

simulated exponential curves convoluted with instrumental response functions.

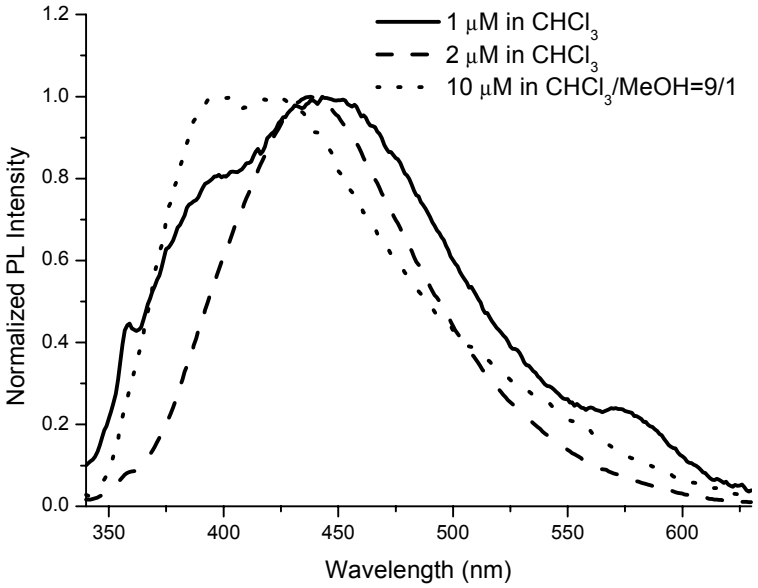
3. X-ray diffractogram of TOBA xerogel



4. Absorption spectra for TOBA samples in monomer (solid) and H-bonded aggregate (dotted) states

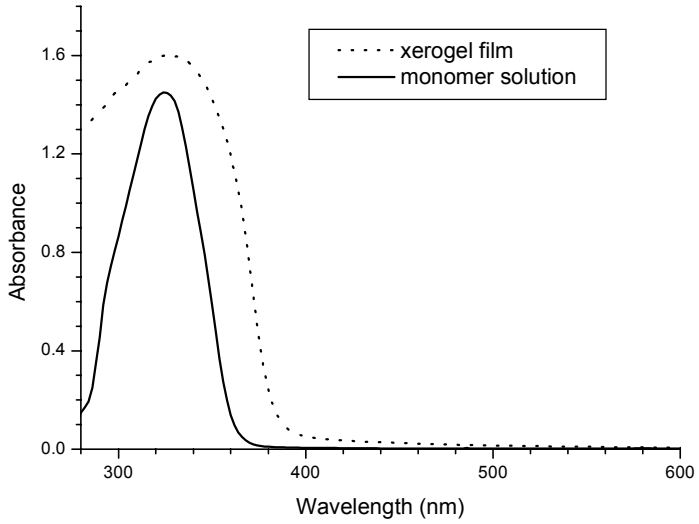


5. Photoluminescence (PL) spectra for TOBA samples in monomer (solid) and H-bonded aggregate (dotted) states

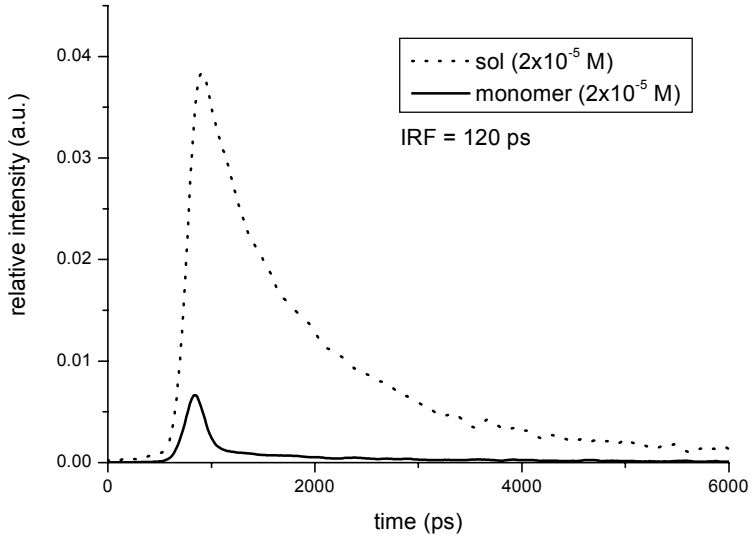


(All samples were heated violently in the capped vial to break the pre-formed aggregation and allowed to stand at room temperature for 1 hour before measurement) PL spectrum of 2-μM $CHCl_3$ solution of TOBA is quite similar ($\lambda_{PL,max}$=438 nm) to that of gel sample in Figure 1d, indicating that the H-bonded aggregate already formed. On the contrary, 1-μM $CHCl_3$ solution shows emission bands from both monomer (400 nm) and H-bonded aggregate (440 nm) states. PL intensity of 2-μM $CHCl_3$ solution is 5 times enhanced relative to that of 1-μM $CHCl_3$ solution. From the results, it is concluded that photoluminescence of TOBA is turned on by H-bond-induced supramolecular aggregation even in the dilute aprotic condition with the critical aggregation concentration (CAC) of around 1 μM in $CHCl_3$.

6. Original data for absorption in Figure 1c



7. Original data for Figure 2



Due to our temporal resolution, the initial amplitude of the fast component within 120 ps is supposed to be observed weaker than the real one. Furthermore, excitation at 386 nm generates smaller excited-state population of a monomer sample than that of a H-bonded aggregate sample because the absorbance at 386 nm is smaller for a monomer than for a H-bonded aggregate.