

Electronic Supplementary Information

for

A new method for fabrication of gel emulsions and its application in preparation of novel porous materials

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Preparation of CDCn

Step 1: In nitrogen atmosphere, THF (50 mL), cholesterol (6 g, 15.5 mmol) and KOH (4.4 g, 78 mmol) were mixed in a round-bottom flask. After the mixture was refluxed for 1 hour, 1,4-dibromo butane (9.2 ml, 78 mmol) was added to the above flask, and then, the reaction mixture was stirred and refluxed for 15 h. After that, the resulting mixture was evaporated to dryness. The residue was washed with water until neutral, and the resulting solid was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 1/1) to give **CBr4** in 35% yield as a white powder. ^1H NMR:($\text{CDCl}_3/\text{Me}_4\text{Si}$, 400Hz): δ (ppm) 5.34(s, 1H, alkenyl), 3.49(t, 2H, OCH_2), 3.44(t, 2H, BrCH_2), 3.12(m, 1H, oxycyclohexyl), 2.34 ~ 0.68(m, 47H, cholesteryl protons, CH_2).

CBr6, **CBr8** and **CBr10** were obtained using the same procedures as **CBr4**. For **CBr6**, ^1H NMR:($\text{CDCl}_3/\text{Me}_4\text{Si}$, 400Hz): δ (ppm) 5.34(s, 1H, alkenyl), 3.45(t, 2H, OCH_2), 3.41(t, 2H, BrCH_2), 3.12(m, 1H, oxycyclohexyl), 2.34 ~ 0.68(m, 51H, cholesteryl protons, CH_2). For **CBr8**, ^1H NMR:($\text{CDCl}_3/\text{Me}_4\text{Si}$, 400Hz): δ (ppm) 5.34(s, 1H, alkenyl), 3.44(t, 2H, OCH_2), 3.40(t, 2H, BrCH_2), 3.11(m, 1H, oxycyclohexyl), 2.34 ~ 0.68(m, 55H, cholesteryl protons, CH_2). For **CBr10**, ^1H NMR:($\text{CDCl}_3/\text{Me}_4\text{Si}$, 400Hz): δ (ppm) 5.35(s, 1H, alkenyl), 3.45(t, 2H, OCH_2), 3.40(t, 2H, BrCH_2), 3.12(m, 1H, oxycyclohexyl), 2.34 ~ 0.68(m, 59H, cholesteryl protons, CH_2).

Step 2: Anhydrous potassium carbonate (1.78 g, 12.88 mmol), dimethyl 5-hydroxyisophthalate (2.70 g, 12.88 mmol) and DMF (20 mL) were added in a round-bottom flask. The mixture was bubbled with nitrogen for 20 minutes. At 65 °C, **CBr4** (3.54 g, 6.44 mmol) was added to the above mixture and the reaction system was further

heated at 80 °C for 9 h. After the reaction, the resulting mixture was poured into ice-water. The precipitate was purified by column chromatography on silica gel (firstly petroleum ether/dichloromethane (1/1), and secondly dichloromethane) to give **CDE4** in 55% yield as a white powder. $^1\text{H NMR}:(\text{CDCl}_3/\text{Me}_4\text{Si}, 400\text{Hz}): \delta(\text{ppm})$ 8.26(s, 1H, benzene), 7.73(s, 2H, benzene), 5.34(s, 1H, alkenyl), 4.07(t, 2H, OCH_2), 3.94(s, 6H, OCH_3), 3.53(t, 2H, OCH_2), 3.14(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 47H, cholesteryl protons, CH_2).

CDE6, **CDE8** and **CDE10** were obtained using the same procedures as **CDE4**. For **CDE6**, $^1\text{H NMR}:(\text{CDCl}_3/\text{Me}_4\text{Si}, 400\text{Hz}): \delta(\text{ppm})$ 8.26(s, 1H, benzene), 7.74(s, 2H, benzene), 5.33(s, 1H, alkenyl), 4.04(t, 2H, OCH_2), 3.94(s, 6H, OCH_3), 3.46(t, 2H, OCH_2), 3.14(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 51H, cholesteryl protons, CH_2).

For **CDE8**, $^1\text{H NMR}:(\text{CDCl}_3/\text{Me}_4\text{Si}, 400\text{Hz}): \delta(\text{ppm})$ 8.26(s, 1H, benzene), 7.74(s, 2H, benzene), 5.34(s, 1H, alkenyl), 4.02(t, 2H, OCH_2), 3.94(s, 6H, OCH_3), 3.45(t, 2H, OCH_2), 3.12(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 55H, cholesteryl protons, CH_2).

For **CDE10**, $^1\text{H NMR}:(\text{CDCl}_3/\text{Me}_4\text{Si}, 400\text{Hz}): \delta(\text{ppm})$ 8.26(s, 1H, benzene), 7.74(s, 2H, benzene), 5.34(s, 1H, alkenyl), 4.03(t, 2H, OCH_2), 3.94(s, 6H, OCH_3), 3.44(t, 2H, OCH_2), 3.13(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 59H, cholesteryl protons, CH_2).

Step 3: **CDE4** (2.4 g, 3.5 mmol) was dissolved in ethyl alcohol (40 ml) in a round-bottom flask, and NaOH (1.42 g, 35 mmol) in 20 mL H_2O was added slowly and the mixture was refluxed for 12 h. After that, the reaction mixture was neutralized with hydrochloric acid (1.5 mol/L) to pH=1 and was cooled at room temperature. The resulted precipitate was filtrated, washed with water for three times and dried to obtain product **CDC4** in 88% yield as a white powder. $^1\text{H NMR}:(\text{DMSO}-d_6/\text{Me}_4\text{Si}, 400\text{Hz}):$

δ (ppm) 13.23(s, 2H, COOH), 8.06(s, 1H, benzene), 7.63(s, 2H, benzene), 5.29(s, 1H, alkenyl), 4.09(t, 2H, OCH₂), 3.46(t, 2H, OCH₂), 3.08(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 47H, cholesteryl protons, CH₂). HRMS (ESI, m/z): Calcd for [(M-H)⁺]: 621.4155. Found: 621.4170.

CDC6, **CDC8** and **CDC10** were obtained using the same procedures as **CDC4**. For **CDC6**, ¹H NMR:(DMSO-*d*₆/Me₄Si, 400Hz): δ (ppm) 13.24(s, 2H, COOH), 8.06(s, 1H, benzene), 7.62(s, 2H, benzene), 5.28(s, 1H, alkenyl), 4.05(t, 2H, OCH₂), 3.40(t, 2H, OCH₂), 3.03(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 51H, cholesteryl protons, CH₂). HRMS (ESI, m/z): Calcd for [(M-H)⁺]: 649.4468. Found: 649.4484. For **CDC8**, ¹H NMR: (DMSO-*d*₆/Me₄Si, 400Hz): δ (ppm) 13.18(s, 2H, COOH), 8.04(s, 1H, benzene), 7.59(s, 2H, benzene), 5.26(s, 1H, alkenyl), 4.02(t, 2H, OCH₂), 3.40(t, 2H, OCH₂), 3.03(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 55H, cholesteryl protons, CH₂). HRMS (ESI, m/z): Calcd for [(M-H)⁺]: 677.4781. Found: 677.4788. For **CDC10**, ¹H NMR:(DMSO-*d*₆/Me₄Si, 400Hz): δ (ppm) 8.02(s, 1H, benzene), 7.55(s, 2H, benzene), 5.21(s, 1H, alkenyl), 3.93(t, 2H, OCH₂), 3.35(t, 2H, OCH₂), 2.96(m, 1H, oxycyclohexyl), 2.36 ~ 0.68(m, 59H, cholesteryl protons, CH₂). HRMS (ESI, m/z): Calcd for [(M-H)⁺]: 705.5094. Found: 705.5096.

General characterizations

A Bruker AVANCF 400 MHz spectrometer was used to measure ¹H NMR data of samples. A Bruker Apex IV FTMS was used to recorded the HRMS data of samples with ESI source. A Shimadzu RF-5301 PC spectrofluorometer was used to recorded the photoluminescent spectra of samples. SEM measurement of samples were conducted on A Scanning Electron Microscopy spectrometer (Hitachi S-3400N II) or a field emission

scanning electron microscope (FEI Nova NanoSEM 450). The laser confocal images of the gel emulsions were taken on an OLYMPUS FV1200 laser confocal microscopy. The elemental distributions were characterized using energy-dispersive X-ray spectroscopy (EDX). TEM measurement of samples were conducted on a Field Transmission Electron Microscopy (FEI Tecnai G2 F20). A Thermo Scientific Nicolette is50 infrared spectrometer was used for performing FT-IR measurements. A ZEISS Axio Observer A1 microscope was used to observe the droplets in the gel emulsions. A Kratos AXIS Ultra X-ray photoelectron spectroscopy was used for collecting XPS data. A TA Q50 thermogravimetric analyzer was used to measure the TG and DTA curves in the flowing N₂ with a temperature ramp rate of 10°C min⁻¹. All rheological measurements were conducted on a stress-controlled rheometer (TA AR-G2). The gap distance was fixed at 1000 µm. A solvent-trapping device was placed over the sample chamber to minimize evaporation. And the measurement temperature was set at 20 °C.

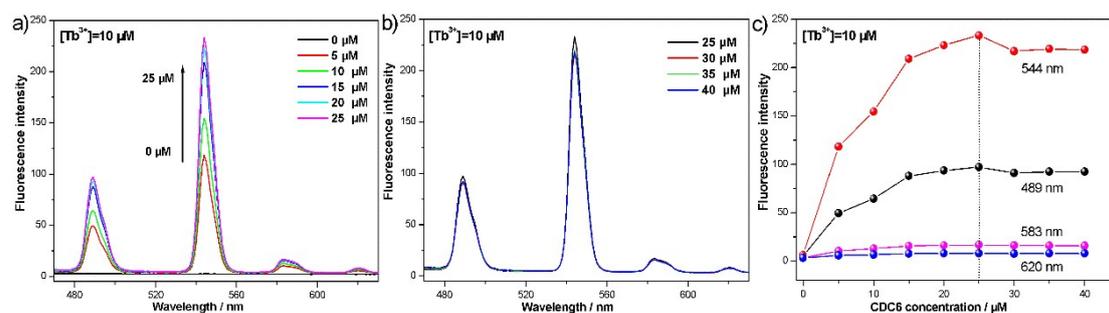


Fig. S1 Emission spectra of 10 μM Tb³⁺ with varied CDC6 concentrations: a) 0-25 μM and b) 25-40 μM. c) Emission intensity of the transition peaks as functions of CDC6 concentration.

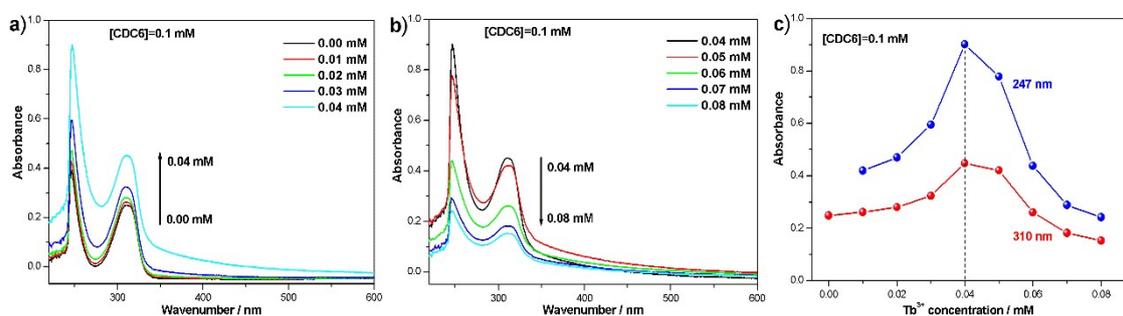


Fig. S2 Absorption spectra of 0.1 mM CDC6 with varied Tb³⁺ concentrations: a) 0-0.04 mM and b) 0.04-0.08 mM. c) Absorbance as functions of Tb³⁺ concentration.

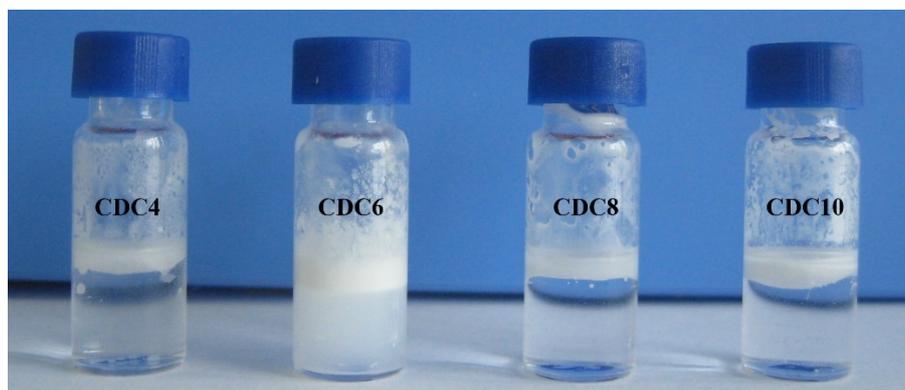
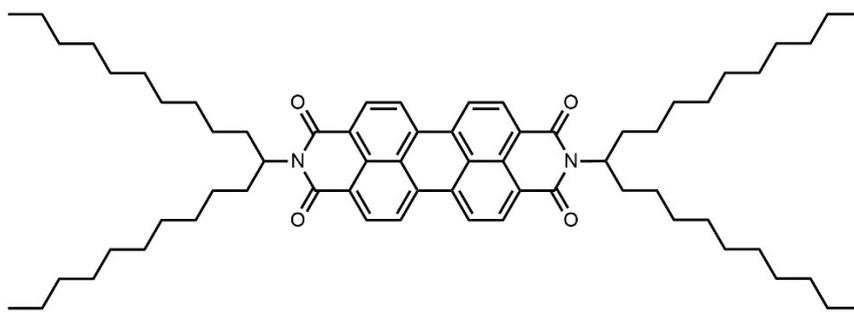


Fig. S3 Photographs of two-phase systems formed by CDCn in *p*-xylene/H₂O without Tb³⁺/Eu³⁺ (*v*:*v*=2:8, [CDCn]=0.0060 mmol mL⁻¹)

Table S1 The effect of oil-water ratio on the formation of gel emulsions ($[\text{CDCn}] = 0.0060 \text{ mmol mL}^{-1}$, $[\text{Tb}^{3+} \text{ or } \text{Eu}^{3+}] = 0.0024 \text{ mmol mL}^{-1}$).

oil-water ratio	CDC4		CDC6	
	<i>p</i> -xylene/H ₂ O	styrene/H ₂ O	<i>p</i> -xylene/H ₂ O	styrene/H ₂ O
4 : 6	E	E	GE	GE
3 : 7	E	E	GE	GE
2 : 8	E	GE	GE	GE
1 : 9	SP	GE	GE	SP

Gel emulsion: GE; Emulsion: E; Separated two phases: SP



Scheme S1 The structure of the fluorescent probe used for fluorescence imaging

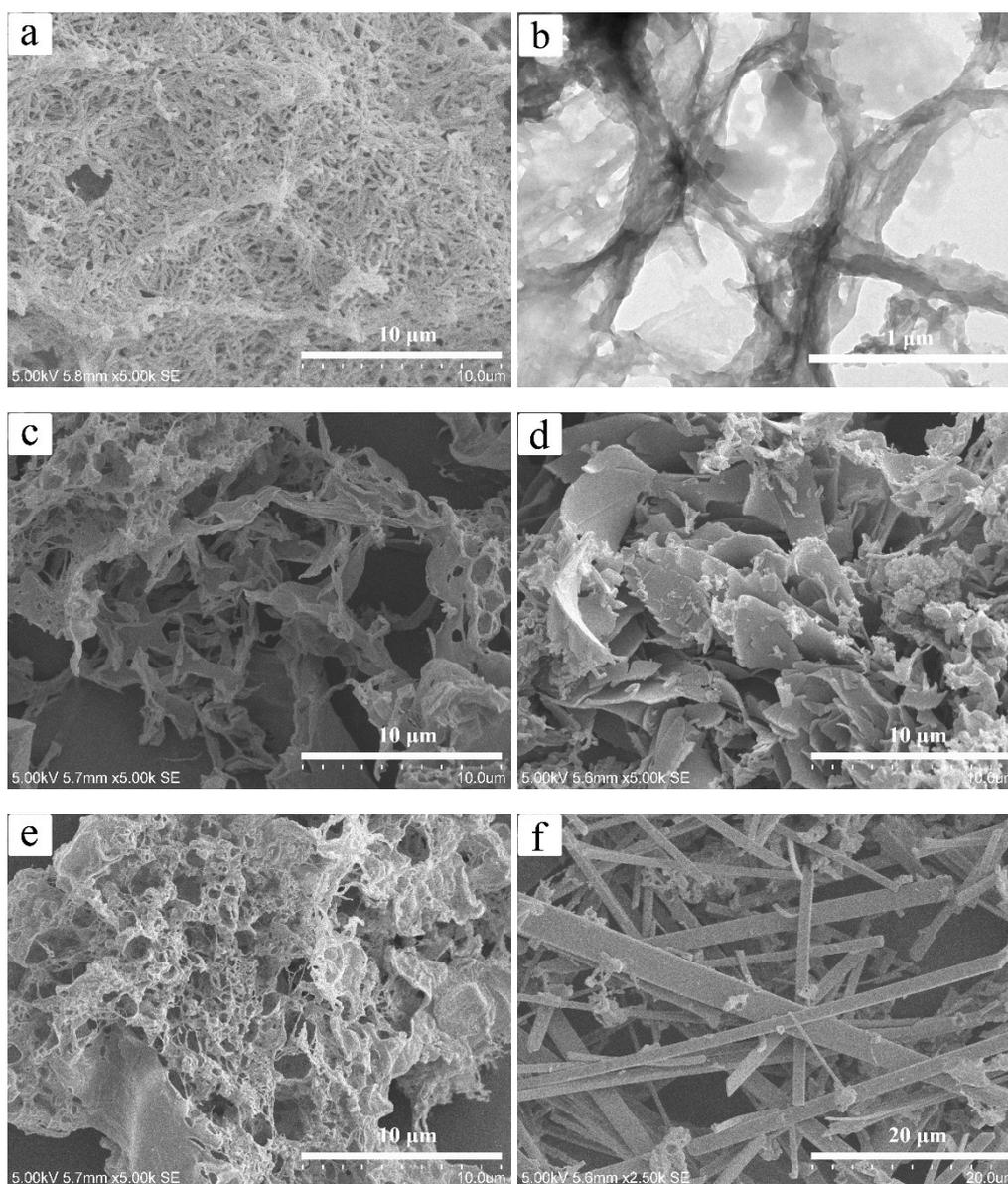


Fig. S4 (a) SEM of $\text{CDC6/Tb(NO}_3)_3$ in benzene/ H_2O ($v:v=2:8$); (b) TEM of $\text{CDC6/Tb(NO}_3)_3$ in benzene/ H_2O ($v:v=2:8$); (c) SEM of $\text{CDC6/Tb(NO}_3)_3$ in toluene/ H_2O ($v:v=2:8$); (d) SEM of $\text{CDC6/Tb(NO}_3)_3$ in *p*-xylene/ H_2O ($v:v=2:8$); (e) SEM of $\text{CDC6/Tb(NO}_3)_3$ in styrene/ H_2O ($v:v=2:8$); (f) SEM of $\text{CDC4/Tb(NO}_3)_3$ in styrene/ H_2O ($v:v=2:8$)

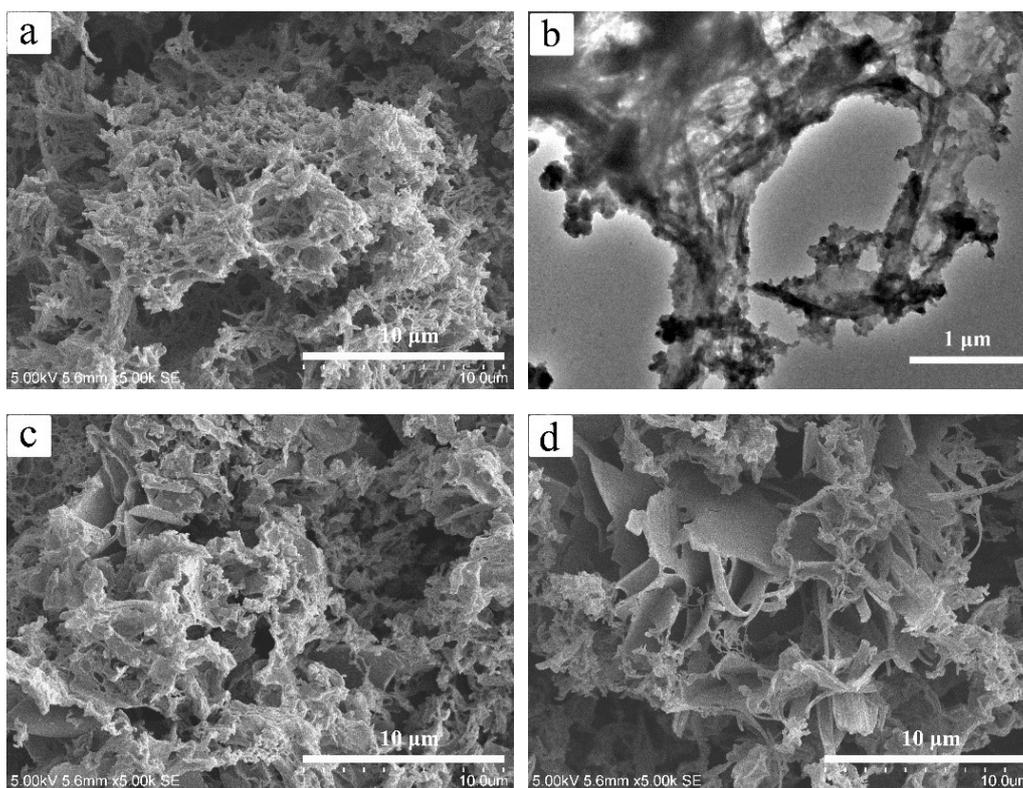


Fig. S5 (a) SEM of $\text{CDC6}/\text{Eu}(\text{NO}_3)_3$ in benzene/ H_2O ($v:v=2:8$); (b) TEM of $\text{CDC6}/\text{Eu}(\text{NO}_3)_3$ in benzene/ H_2O ($v:v=2:8$); (c) SEM of $\text{CDC6}/\text{Eu}(\text{NO}_3)_3$ in toluene/ H_2O ($v:v=2:8$); (d) SEM of $\text{CDC6}/\text{Eu}(\text{NO}_3)_3$ in styrene/ H_2O ($v:v=2:8$)

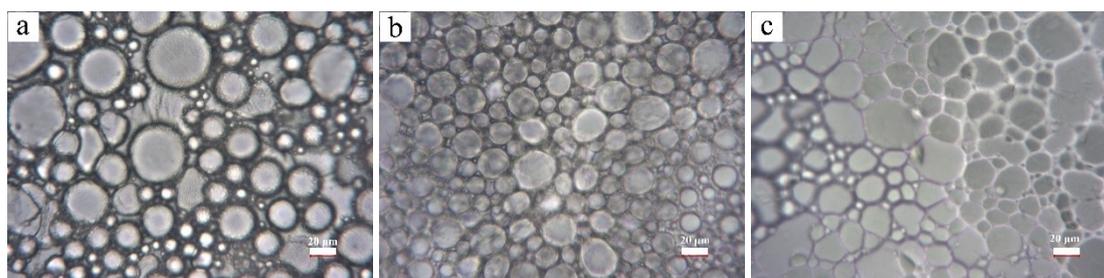


Fig. S6 Optical micrographs of $\text{CDC6/Tb}(\text{NO}_3)_3$ in p -xylene/ H_2O , and the volume ratio of styrene to water was: (a) 4:6; (b) 3:7; (c) 2:8

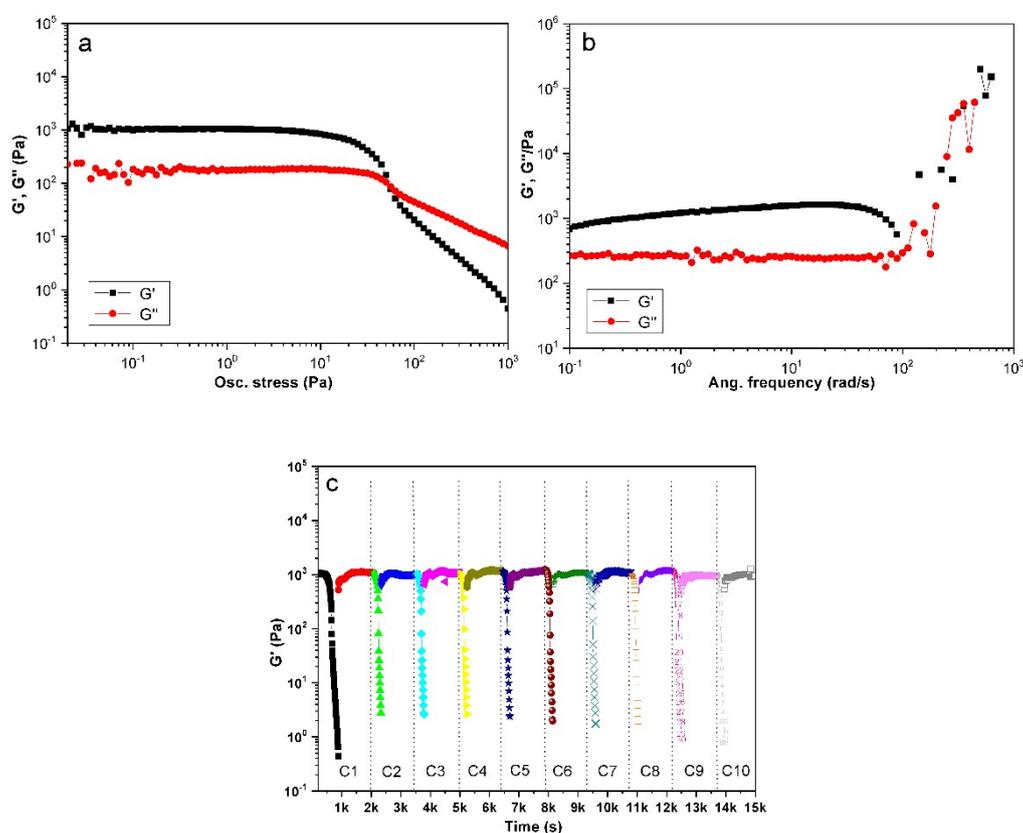


Fig. S7 For the gel emulsion of $\text{CDC6/Eu}(\text{NO}_3)_3$ in p -xylene/ H_2O $\{\nu:\nu=2:8, [\text{CDC6}]=0.0060 \text{ mmol mL}^{-1}, [\text{Eu}(\text{NO}_3)_3]=0.0024 \text{ mmol mL}^{-1}\}$: (a) Evolution of G' and G'' as functions of the applied shear stress; (b) Evolution of G' and G'' as functions of the frequency; (c) Reversibility of the thixotropic property examined via alternative stress and time sweeps. C_x refer to the x^{th} time circle, and $x = 1-10$.

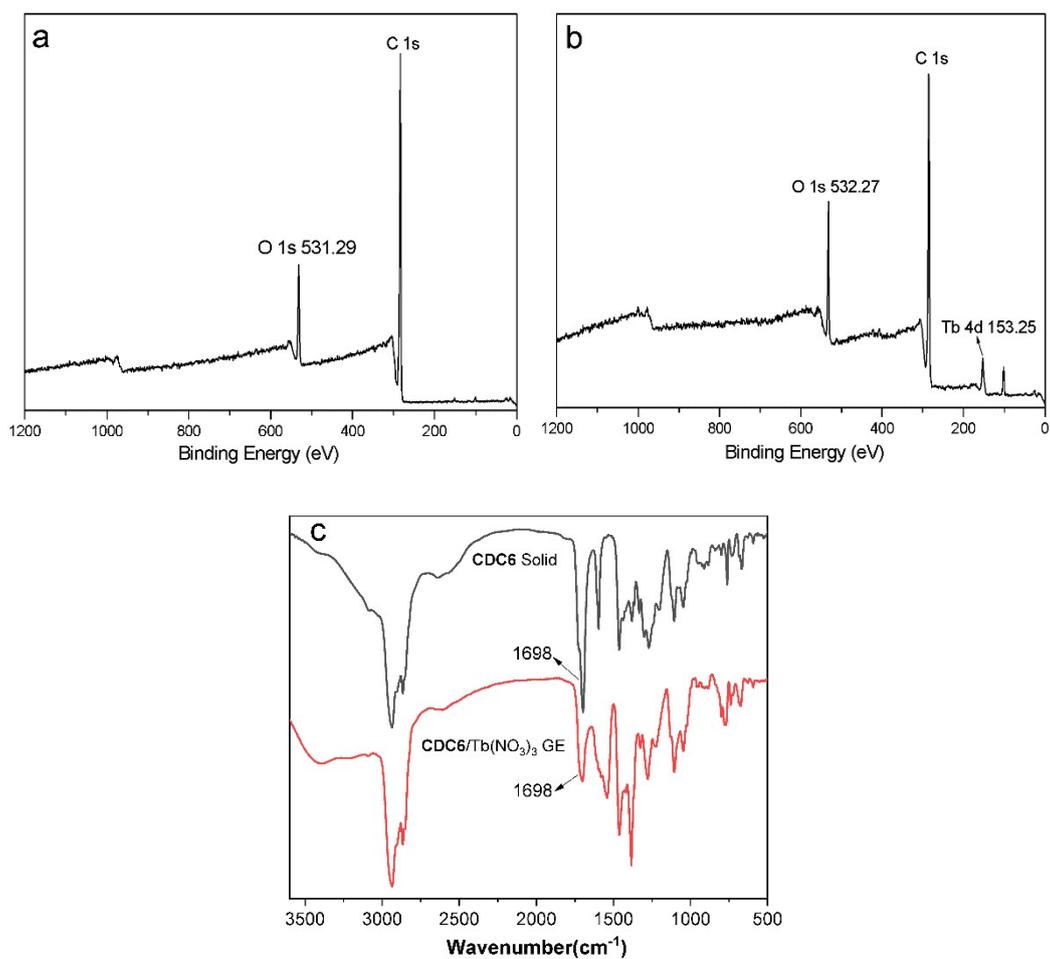


Fig. S8 XPS wide spectrum of (a) **CDC6** and (b) the **CDC6/Tb(NO₃)₃** gel emulsion in *p*-xylene/H₂O; (c) FTIR spectra of **CDC6** and the **CDC6/Tb(NO₃)₃** gel emulsion in *p*-xylene/H₂O.

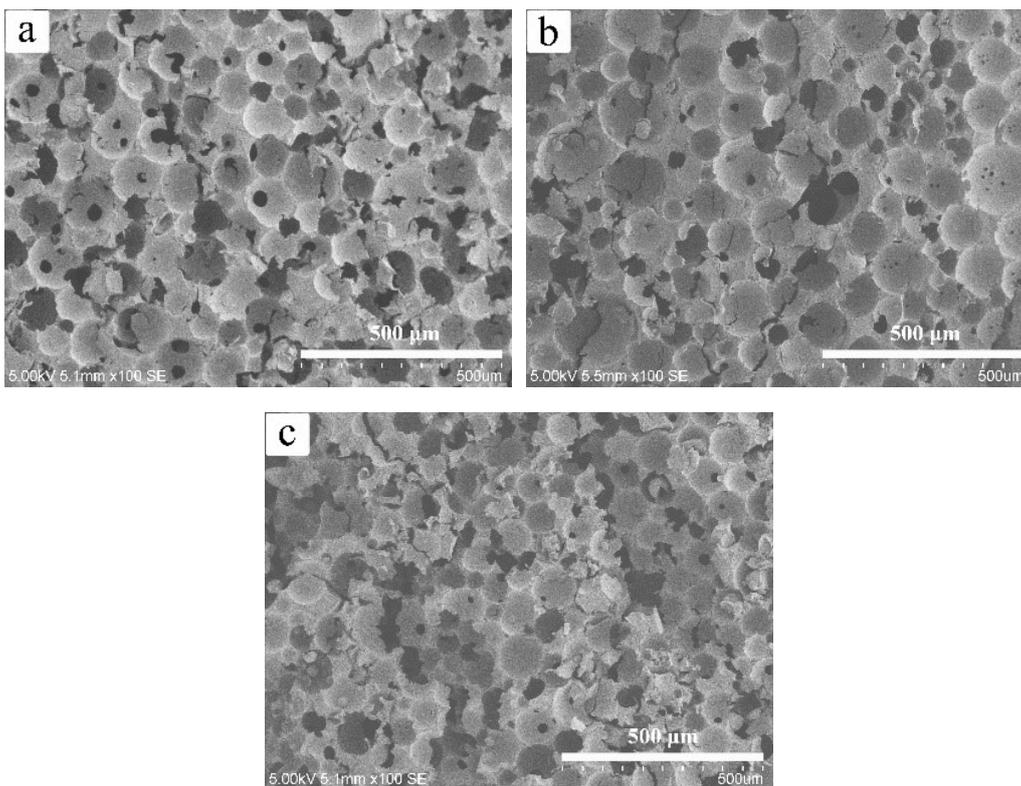


Fig. S9 SEM images of porous monoliths prepared by polymerization of gel emulsions of **CDC6**/ $\text{Tb}(\text{NO}_3)_3$ in styrene/ H_2O ($v:v=2:8$) with different concentration of DVB in styrene: (a) 5%; (b) 10%; (c) 15%.

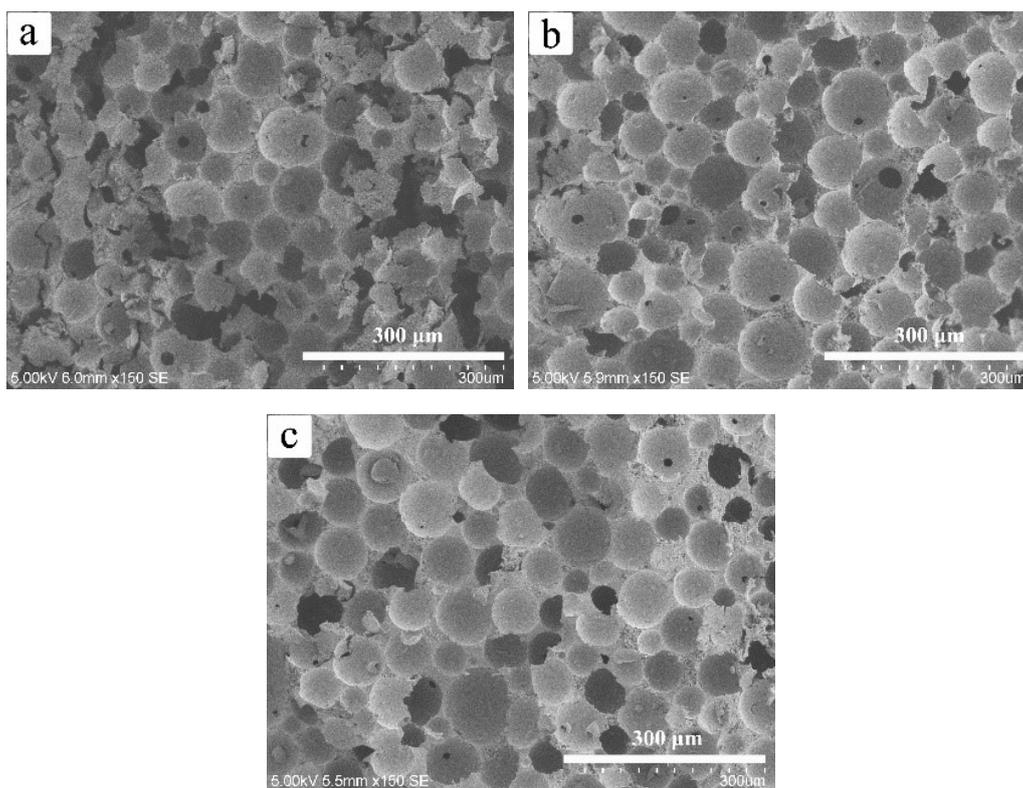


Fig. S10 SEM images of porous monoliths prepared by polymerization of the gel emulsions of **CDC6**/ $\text{Tb}(\text{NO}_3)_3$ in styrene/ H_2O ($v:v=2:8$) with different concentration of **CDC6**/ $\text{Tb}(\text{NO}_3)_3$ in styrene: (a) $[\text{CDC6}]=0.0030 \text{ mmol mL}^{-1}$, $[\text{Tb}^{3+}]=0.0012 \text{ mmol mL}^{-1}$; (b) $[\text{CDC6}]=0.0060 \text{ mmol mL}^{-1}$, $[\text{Tb}^{3+}]=0.0024 \text{ mmol mL}^{-1}$; (c) 10%; (c) $[\text{CDC6}]=0.0090 \text{ mmol mL}^{-1}$, $[\text{Tb}^{3+}]=0.0036 \text{ mmol mL}^{-1}$.

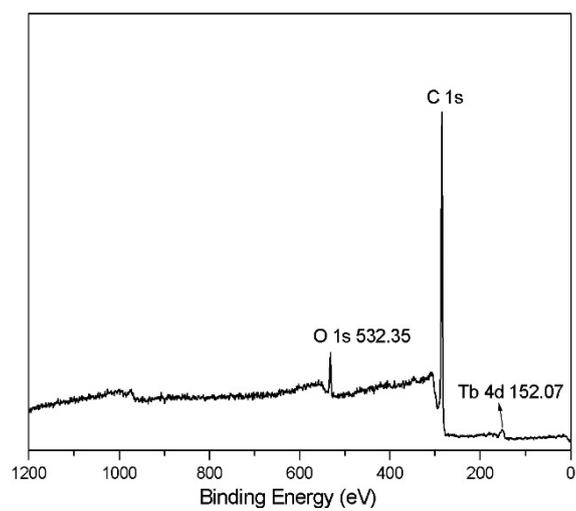


Fig. S11 XPS wide spectrum of the porous material prepared by polymerization of CDC6/Tb(NO₃)₃/ styrene/H₂O gel emulsion.

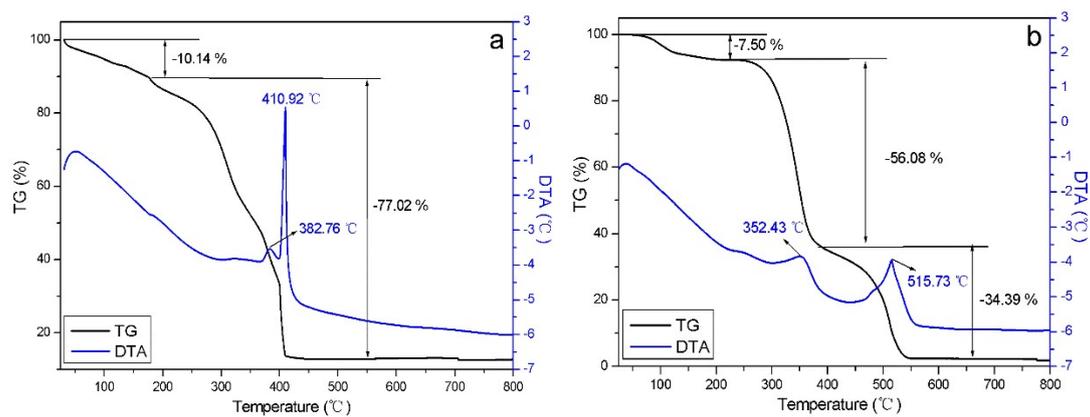


Fig. S12 The TG-DTA curve of (a) CDC6/Tb(NO₃)₃/p-xylene/H₂O gel emulsion and (b) the porous material prepared by polymerization of CDC6/Tb(NO₃)₃/styrene/H₂O gel emulsion.