Electronic Supplementary Information

Dynamic Monitoring of Self-Assembly by Confining Conformational Changes of Butterfly-Motion-Based Molecules

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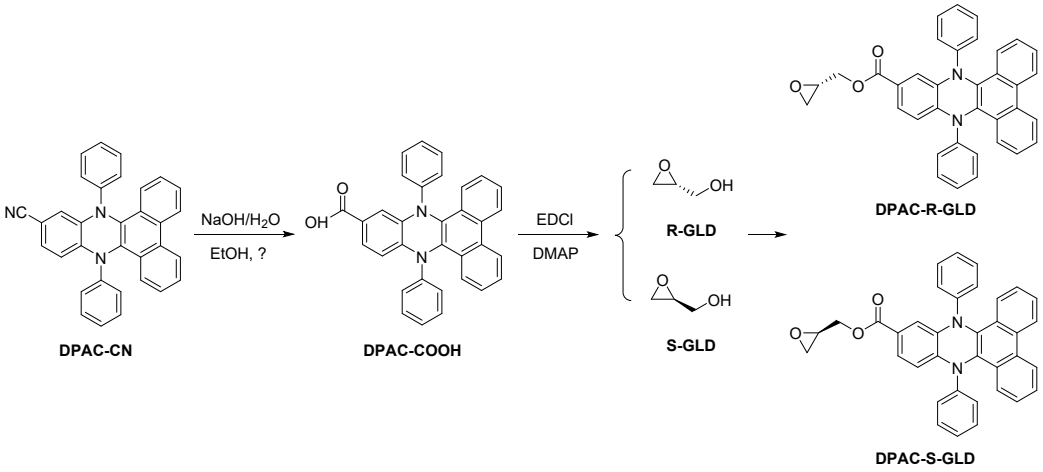
1. Materials and General Methods

All regents and solvents were purchased from chemical suppliers and used without further purification. The molecular structures were confirmed by ^{1}H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy. Compound **DPAC-CN** was synthesized according to our previous work[1]. Other chemicals used for the synthesis were of reagent grade without further purification. Water used in tests was ultrapure. The UV-Vis absorption and PL spectra were performed on a SHIMADZU UV-2600 and a SHIMADZU RF-6000 spectrophotometer at 25 ^{o}C, respectively. DLS was carried out on a Malvern analytical Nano ZSE ZEN-3700 at 25 ^{o}C. Circularly polarized luminescence (CPL) spectra were measured using the JASCO CPL-300 spectrofluoropolarimeter. Circular dichroism (CD) spectra were obtained using the JASCO J-815 CD spectrophotometer. Spectroscopic grade solvents were used for performing all the tests. SEM images were obtained by using a S-3400N (droplets of the sample solution (1×10^{-4} M) were applied to a silicon slice and dried in air at room temperature, and then coated with nano Au in a vacuum). Fluorescence decay curve were recorded on Edinburgh-Steady state/Transient fluorescence spectrometer FLS1000.

2. Details of the synthetic procedures



Scheme. S1 Synthetic route of compounds **DPAC-R/S-GLD**.

9,14-diphenyl-9,14-dihydrodibenzo[*a*,*c*]phenazine-11-carboxylic acid (**DPAC-COOH**): 9,14-diphenyl-9,14-dihydrodibenzo[*a*,*c*]phenazine-11-carbonitrile (**DPAC-CN**) (1.0 g, 2.17 mmol) was dispersed in 200 mL of ethanol. Afterwards, 40 mL of 20% aqueous sodium hydroxide was added into the reaction mixture. The solution was heated to reflux for 12 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum. Then diluted hydrochloric acid solution was added to acidify the mixture and afford the white solid. The product was filtered and washed thoroughly by water and dried under vacuum to give faint yellow solid (970 mg, 93%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.19 (s, 1H), 8.94 (d, J = 8.4 Hz, 2H), 8.31 (d, J = 1.8 Hz, 1H), 8.05 – 8.02 (m, 2H), 7.98 (dd, J = 8.2, 1.8 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.16 – 7.11 (m, 6H), 6.99 (d, J = 8.2 Hz, 2H), 6.95 – 6.91 (m, 1H), 6.88 (t, J = 7.2 Hz, 1H). ^{13}C NMR (151 Hz, DMSO-d_6) δ: 166.65, 148.92, 147.37, 146.58, 143.16, 136.38, 136.20, 129.70, 129.49, 129.23, 129.19, 128.27, 127.94, 127.51, 127.46, 127.26, 127.14, 127.01, 125.98, 123.79, 123.76, 123.66, 122.69, 121.86, 118.70, 117.05. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{33}H_{23}N_2O_2$, 479.1760; found, 479.1756.

(R)-oxiran-2-ylmethyl-9,14-diphenyl-9,14-dihydrodibenzo[*a*,*c*]phenazine-11-carboxylate (**DPAC-R-GLD**): In a flame-dried round bottom flask, **DPAC-COOH** (200 mg, 0.42 mmol) and **R-GLD** (154 mg, 128 μL, 2.08 mmol) were dispersed into 150 mL DCM. Then EDC·HCl (80 mg, 0.42 mmol) and DMAP (255 mg, 2.08 mmol) were added to give a transparent yellow solution. After stirring at room temperature for 12 h, the solution was quenched with aqueous 1M HCl and extracted with DCM. The resulting organic phase was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica (DCM: EA = 5: 1) to give a white solid (145 mg, 65%). **DPAC-R-GLD**: ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.96 – 8.92 (m, 2H), 8.35 (d, J = 1.8 Hz,

1H), 8.09 – 8.05 (m, 2H), 8.02 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.65 – 7.62 (m, 1H), 7.59 – 7.55 (m, 1H), 7.16 – 7.11 (m, 6H), 6.99 – 6.93 (m, 3H), 6.88 (t, *J* = 7.2 Hz, 1H), 4.71 (dd, *J* = 12.2, 2.6 Hz, 1H), 4.15 (dd, *J* = 12.2, 6.4 Hz, 1H), 3.42 – 3.38 (m, 1H), 2.87 (t, *J* = 4.6 Hz, 1H), 2.78 (dd, *J* = 5.0, 2.6 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: 164.84, 149.15, 147.45, 146.43, 143.11, 136.35, 136.03, 129.76, 129.49, 129.28, 129.20, 128.30, 127.85, 127.57, 127.50, 127.26, 127.05, 126.30, 125.95, 123.82, 123.77, 123.65, 122.97, 121.88, 119.09, 116.91, 65.70, 49.07, 43.91. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{36}H_{27}N_2O_3$, 535.2022; found, 535.2021.

(S)-oxiran-2-ylmethyl-9,14-diphenyl-9,14-dihydrodibenzo[*a*,*c*]phenazine-11-carboxylate (**DPAC-S-GLD**): In a flame-dried round bottom flask, **DPAC-COOH** (200 mg, 0.42 mmol) and **S-GLD** (154 mg, 128 μL, 2.08 mmol) were dispersed into 150 mL of DCM. Then EDC·HCl (80 mg, 0.42 mmol) and DMAP (255 mg, 2.08 mmol) were added to give a transparent yellow solution. After stirring at room temperature for 12 h, the solution was quenched with aqueous 1M HCl and extracted with DCM. The resulting organic phase was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica (DCM: EA = 5: 1) to give a white solid (142 mg, 64%). **DPAC-S-GLD**: ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.94 (d, *J* = 8.2 Hz, 2H), 8.35 (d, *J* = 1.8 Hz, 1H), 8.09 – 8.05 (m, 2H), 8.02 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.66 – 7.62 (m, 1H), 7.59 – 7.55 (m, 1H), 7.16 – 7.11 (m, 6H), 6.99 – 6.93 (m, 3H), 6.88 (t, *J* = 7.2 Hz, 1H), 4.71 (dd, *J* = 12.4, 2.6 Hz, 1H), 4.15 (dd, *J* = 12.4, 6.4 Hz, 1H), 3.42 – 3.39 (m, 1H), 2.87 (t, *J* = 4.6 Hz, 1H), 2.78 (dd, *J* = 5.0, 2.6 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: 164.83, 149.03, 147.44, 146.43, 143.11, 136.34, 136.03, 129.76, 129.49, 129.28, 129.20, 128.30, 127.84, 127.56, 127.51, 127.25, 127.02, 126.29, 125.95, 123.81, 123.77, 123.65, 122.96, 121.88, 119.09, 116.91, 65.70, 49.07, 43.91. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{36}H_{27}N_2O_3$, 535.2022; found, 535.2020.

3. Supplementary dates for additional optical properties

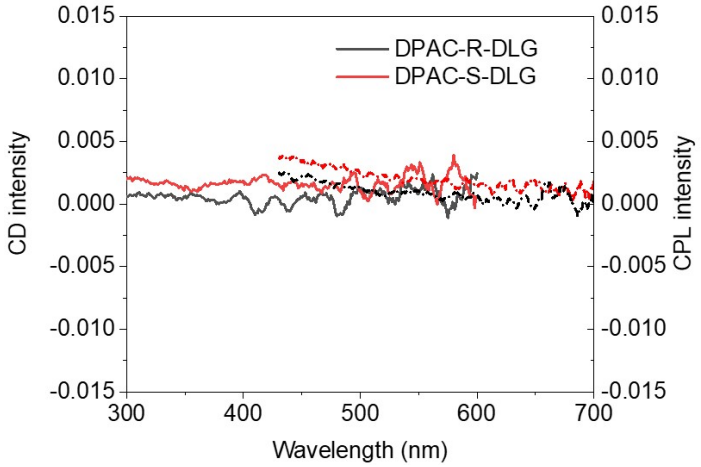


Fig. S1 The CD spectra (solid line) and CPL spectra (dash line) of compounds **DPAC-R/S-GLD** in THF (10^{-5} M, λ_{ex} = 340 nm), respectively.

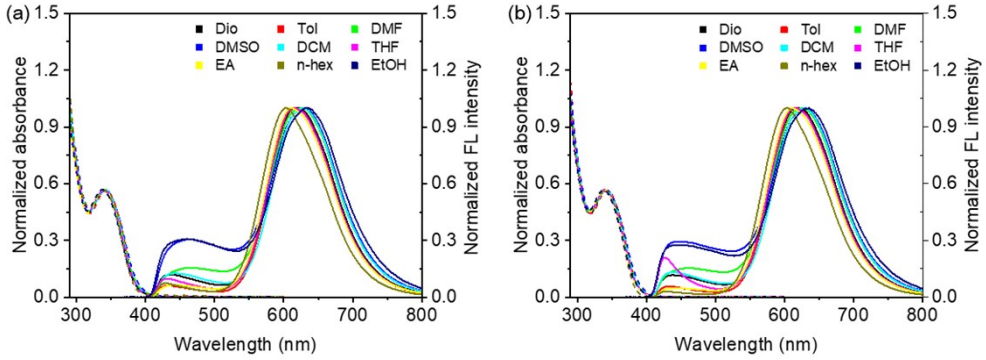


Fig. S2 The normalized UV-visible absorption and emission spectra of compounds **DPAC-R/S-GLD** in different solvents, λ_{ex} = 340 nm.

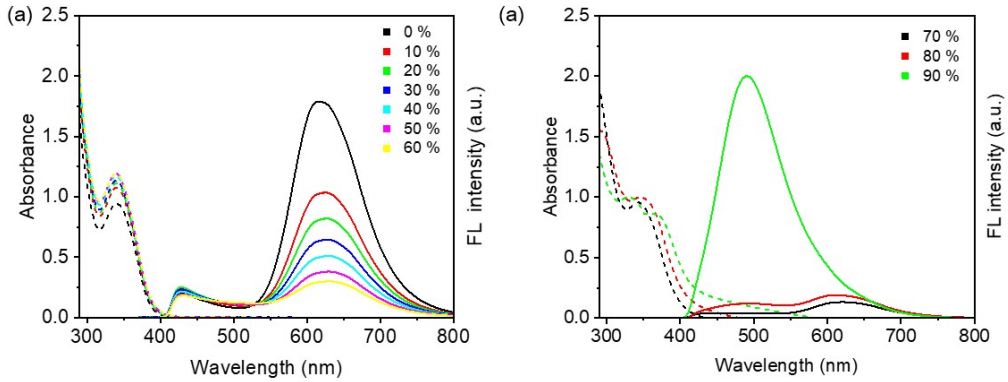


Fig. S3 The UV-visible absorption and emission spectra of **DPAC-S-GLD** in different H_2O/THF mixtures with f_w from (a) 0% to 60% and (b) 70% to 90% at 298 K (10^{-4} M, λ_{ex} = 340 nm).

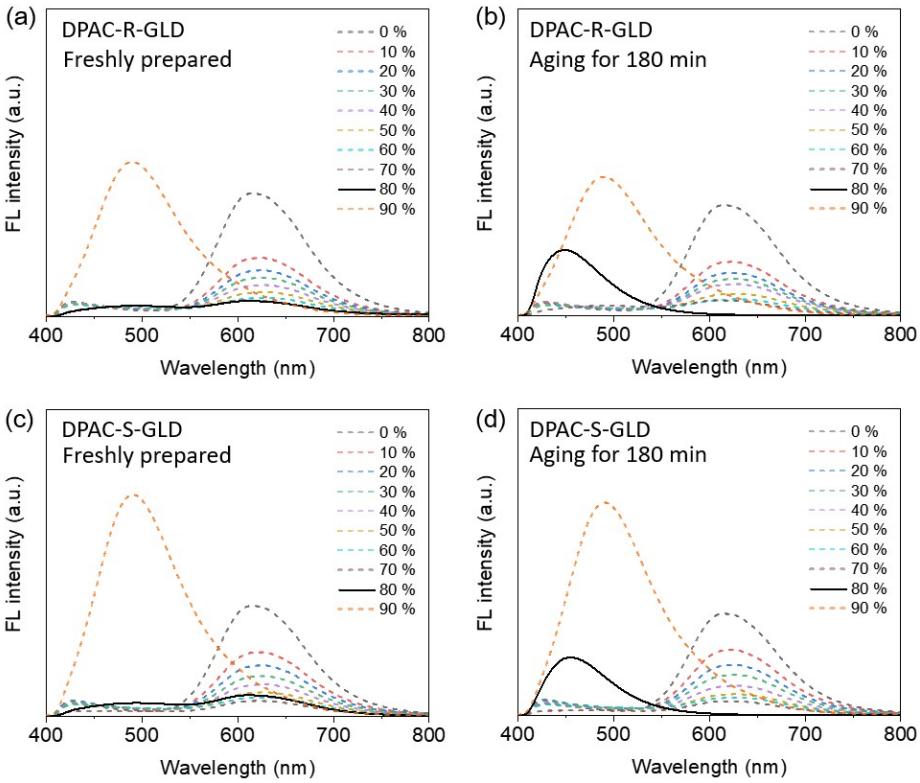


Fig. S4 Emission spectra of (a, c) freshly prepared and (b, d) 180 min aging **DPAC-R/S-GLD** in different THF/H_2O (v/v) solutions at 298 K (10^{-4} M, λ_{ex} = 340 nm), respectively.

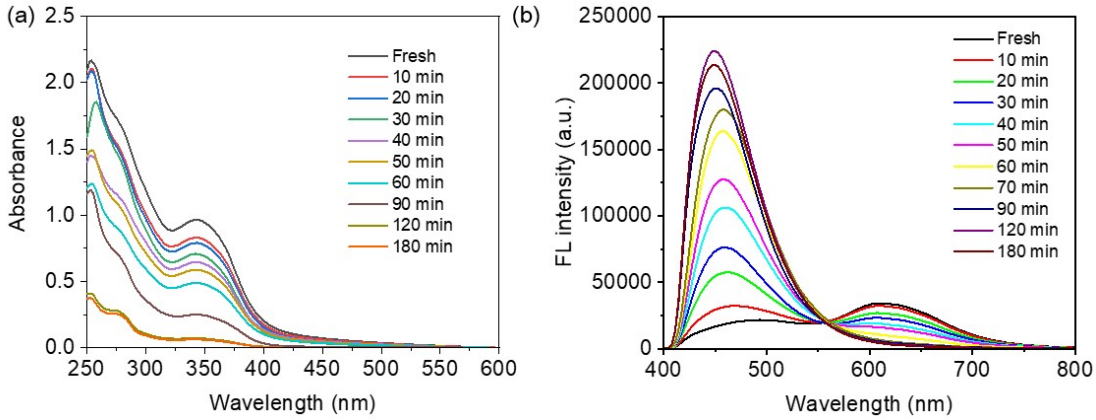


Fig. S5 Time-dependent (a) UV-visible absorption and (b) emission spectra of **DPAC-R-GLD** (10^{-4} M) in H_2O/THF solution (f_w = 80%) at 298 K, respectively, λ_{ex} = 340 nm.

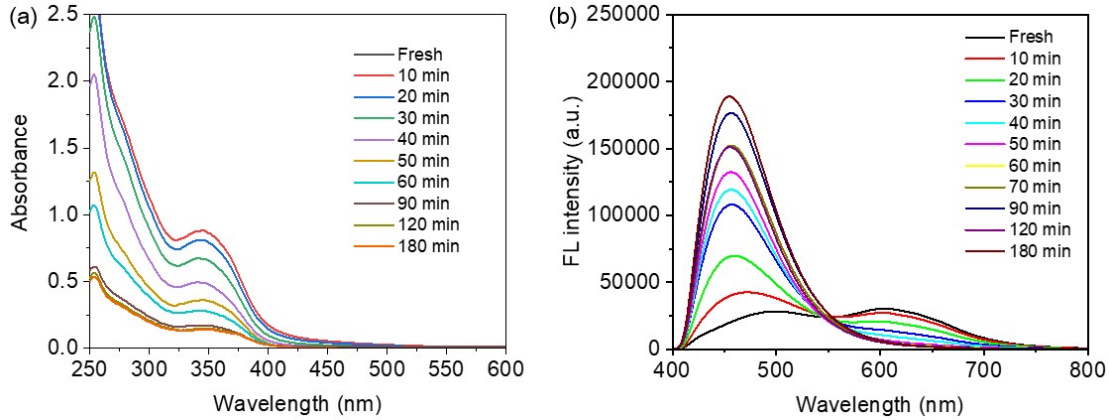


Fig. S6 Time-dependent (a) UV-visible absorption and (b) emission spectra of **DPAC-S-GLD** (10^{-4} M) in H_2O/THF solution (f_w = 80%) at 298 K, respectively, λ_{ex} = 340 nm.

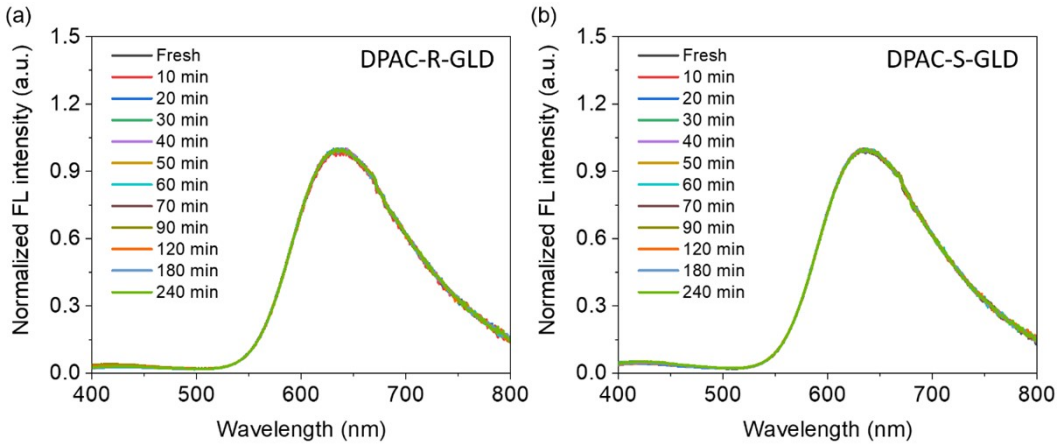


Fig. S7 Time-dependent emission spectra of **DPAC-R/S-GLD** (10^{-4} M) in THF solution, respectively, λ_{ex} = 340 nm.

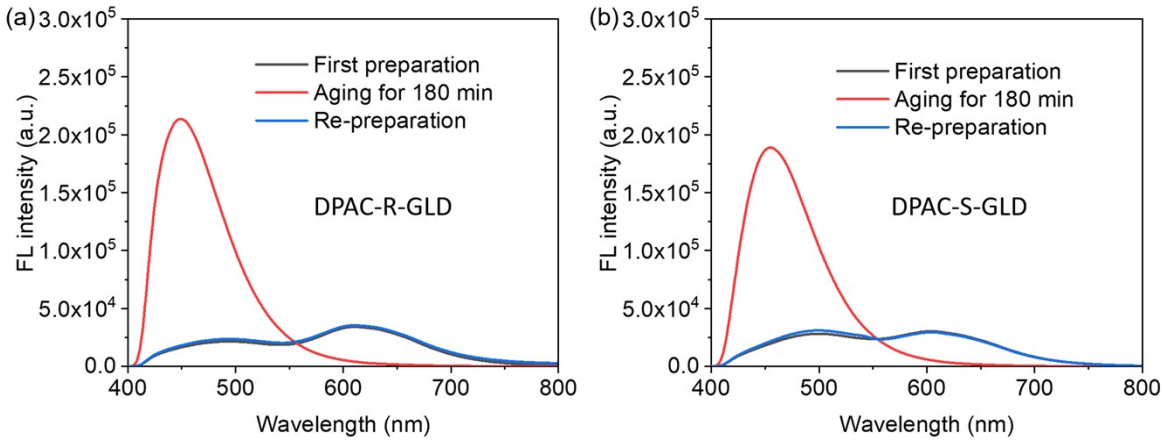


Fig. S8 Emission spectra of (a) **DPAC-R-GLD** and (b) **DPAC-S-GLD** in H_2O/THF solution (f_w = 80%) at 298 K under different conditions: fresh preparation; after aging for 180 min; re-preparation from aggregates extract (λ_{ex} = 340 nm).

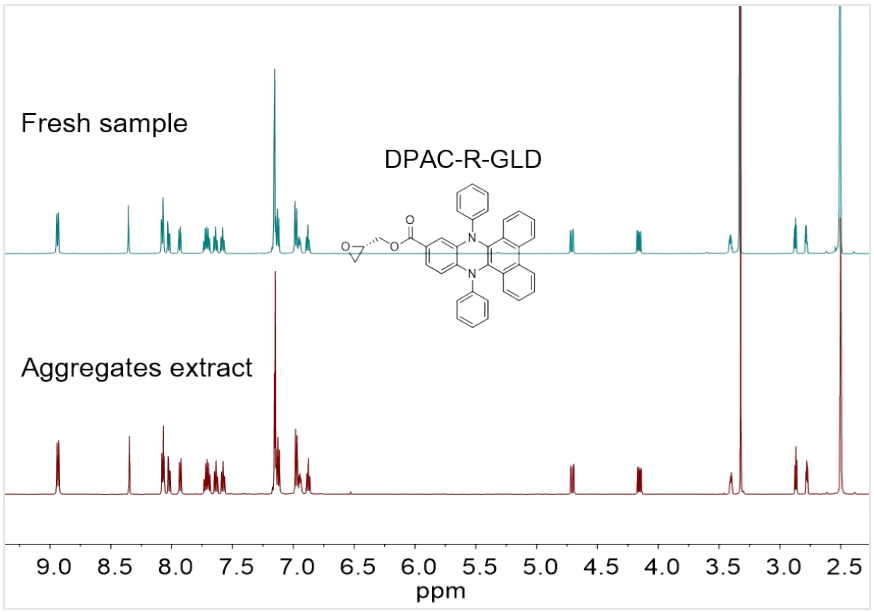


Fig. S9 ^{1}H NMR (600 MHz) spectra of fresh sample (upper) and aggregates extract (down) of **DPAC-R-GLD** in DMSO-d_6. The aggregates extract is from **DPAC-R-GLD** in H_2O/THF solution (f_w = 80%) after aging for 240 min at 298 K.

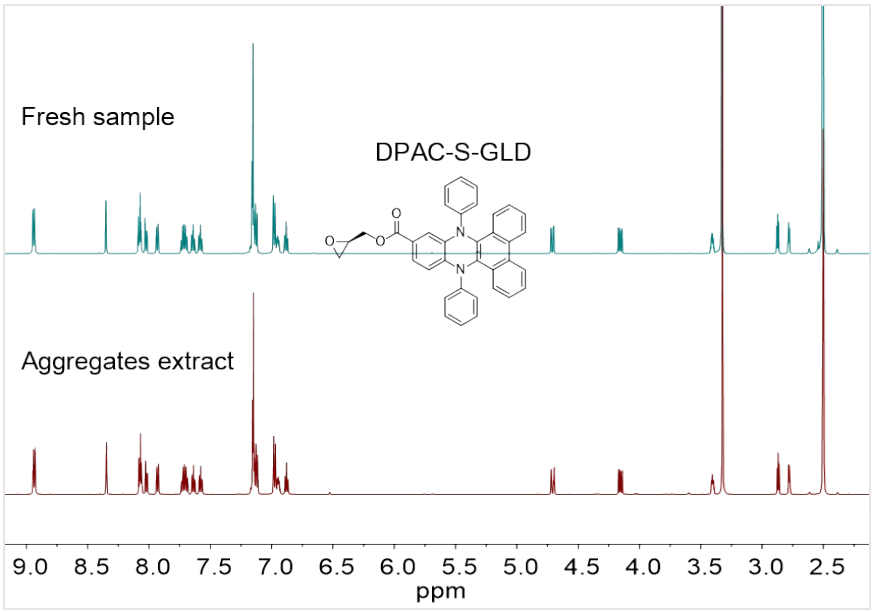


Fig. S10 ^{1}H NMR (600 MHz) spectra of fresh sample (upper) and aggregates extract (down) of **DPAC-S-GLD** in DMSO-d_6. The aggregates extract is from **DPAC-S-GLD** in H_2O/THF solution (f_w = 80%) after aging for 240 min at 298 K.

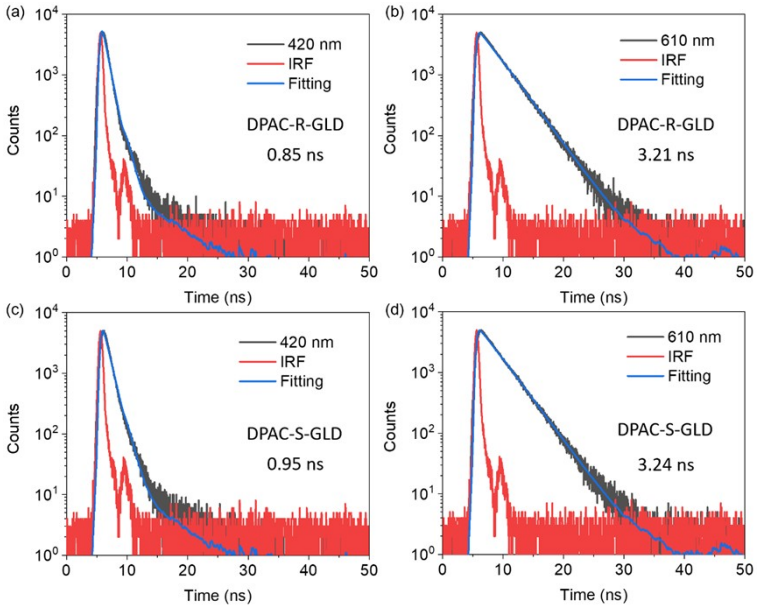


Fig. S11 Fluorescence lifetime and fitting results of (a) **DPAC-R-GLD** and (c) **DPAC-S-GLD** at 420 nm, respectively. Fluorescence lifetime and fitting results of (b) **DPAC-R-GLD** and (d) **DPAC-S-GLD** at 610 nm, respectively. The concentration of compounds is 10^{-5} M in THF at 298 K. λ_{ex}=375 nm.

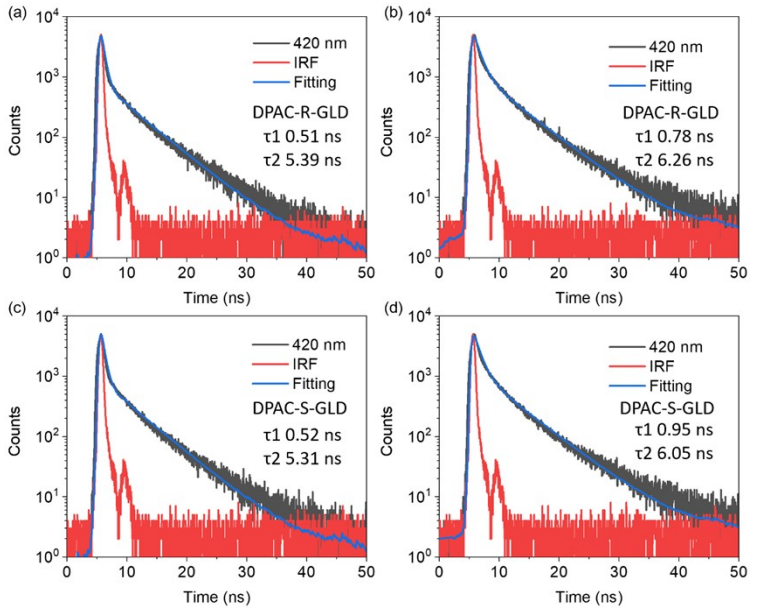


Fig. S12 Fluorescence lifetime and fitting results of newly prepared (a) **DPAC-R-GLD** and (c) **DPAC-S-GLD** at 420 nm with the concentration of 10^{-4} M in H_2O/THF solution (f_w = 80%) at 298 K, respectively, λ_{ex}=375 nm. Fluorescence lifetime and fitting results of (b) **DPAC-R-GLD** and (d) **DPAC-S-GLD** at 420 nm after aging for 180 min with the concentration of 10^{-4} M in H_2O/THF solution (f_w = 80%) at 298 K, respectively, λ_{ex}=375 nm.

Table S1 Quantum yields of fresh **DPAC-R/S-GLD** in H_2O/THF (v/v) solutions with different water fraction at 298K.

Water (%)	0	10	20	30	40	50	60	70	80	90
Overall quantum yield (**DPAC-R-GLD**)	7.1	3.3	2.2	1.2	0.8	0.6	0.5	0.5	0.8	15.7
Overall quantum yield (**DPAC-S-GLD**)	7.0	3.1	2.1	1.4	0.6	0.7	0.5	0.5	0.7	15.5

Table S2 Time-dependent quantum yields of **DPAC-R/S-GLD** in H_2O/THF solution (f_w = 80%) at 298 K (1×10^{-4} M, λ_{ex} = 340 nm).

Time (min)	Fresh	30	60	90	120	180
Quantum yield (**DPAC-R-GLD**)	0.8	2.3	7.9	8.2	9.6	11.7
Quantum yield (**DPAC-S-GLD**)	0.7	2.1	7.7	8.3	8.8	10.6

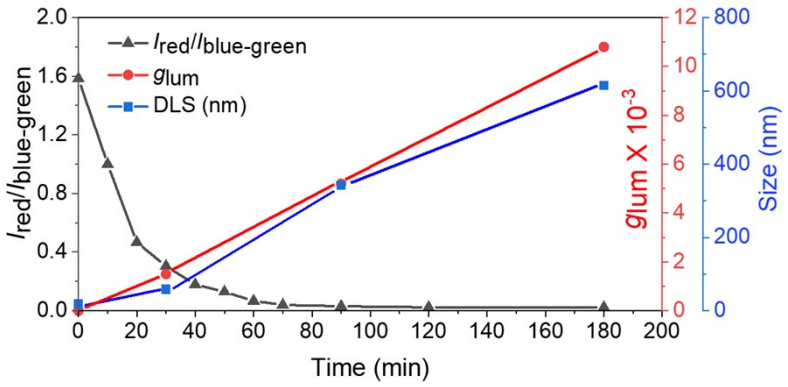


Fig. S13 Time-dependent $I_{Red}/I_{Blue\text{-}Green}$, g_{lum} and DLS of **DPAC-R-GLD** in H_2O/THF solution (f_w = 80%), respectively. DLS and g_{lum} can be fitted by a suitable formula Y = 0.017X-0.019, R^2 = 0.99.

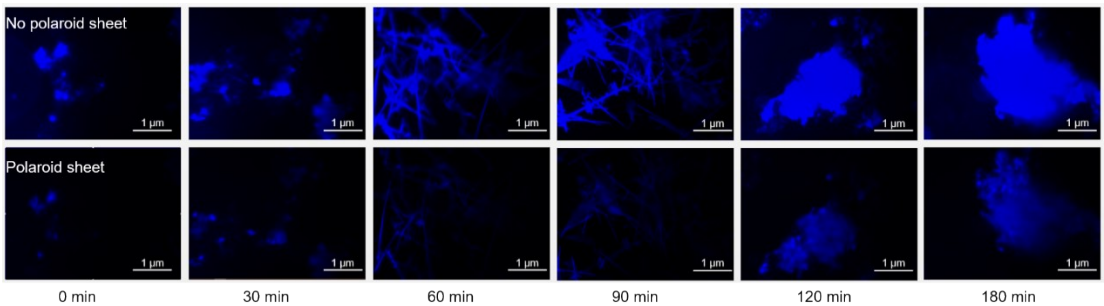


Fig. S14 Time-dependent fluorescence images of **DPAC-R-GLD** in H_2O/THF solution (f_w = 80%) with and without polaroid sheet, respectively.

Table. S3 Mean fluorescence intensity of time-dependent fluorescence images of **DPAC-R-GLD** in H_2O/THF solution (f_w = 80%) with and without polaroid sheet.

	0	30	60	90	120	180
No Sheet	1071	1298	2005	2126	2469	3273
With Sheet	191	213	384	443	725	1001

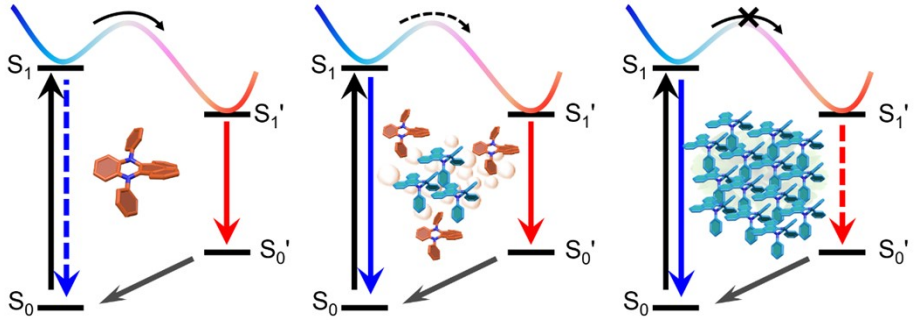


Fig. S15 Illustration of the morphological transition and corresponding energy diagram of **DPAC-R/S-GLD** in different states.

4. Supplementary dates for additional structure properties

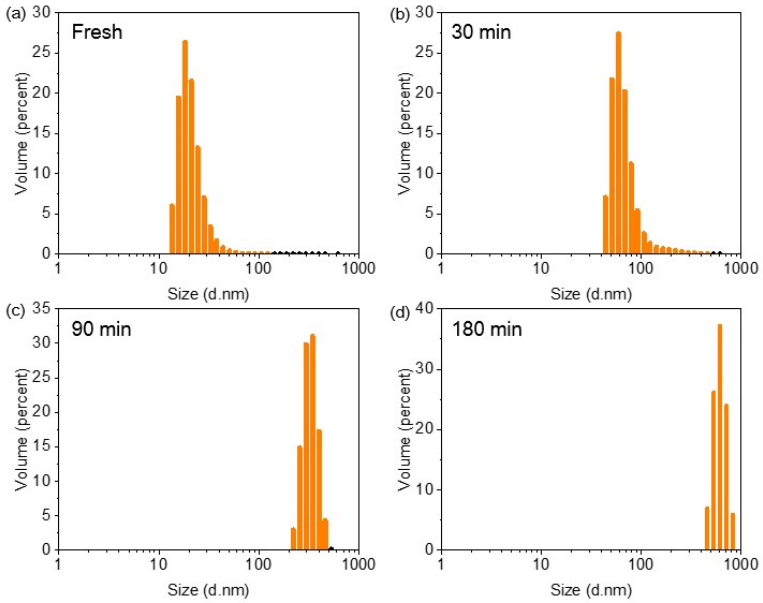


Fig. S16 Time-dependent dynamic light scattering data of **DPAC-R-GLD** (10^{-4} M) in H_2O/THF solution (f_w = 80%) at 298 K.

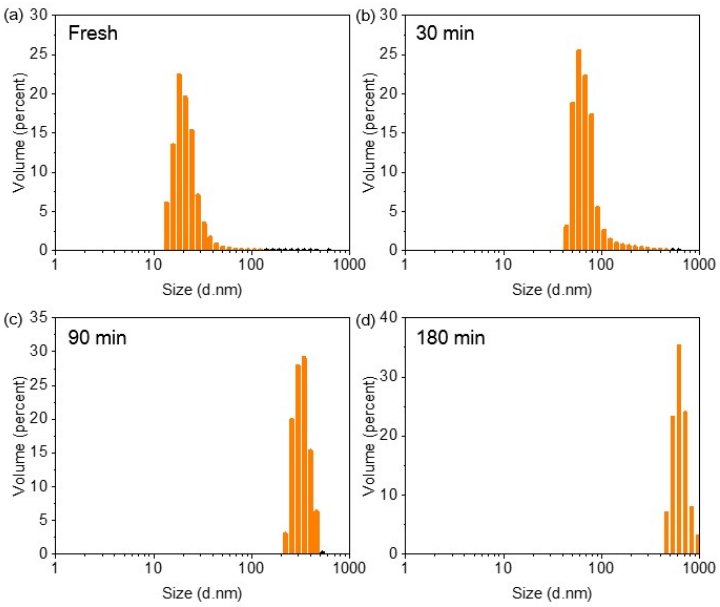


Fig. S17 Time-dependent dynamic light scattering data of **DPAC-S-GLD** (10^{-4} M) in H_2O/THF solution (f_w = 80%) at 298 K.

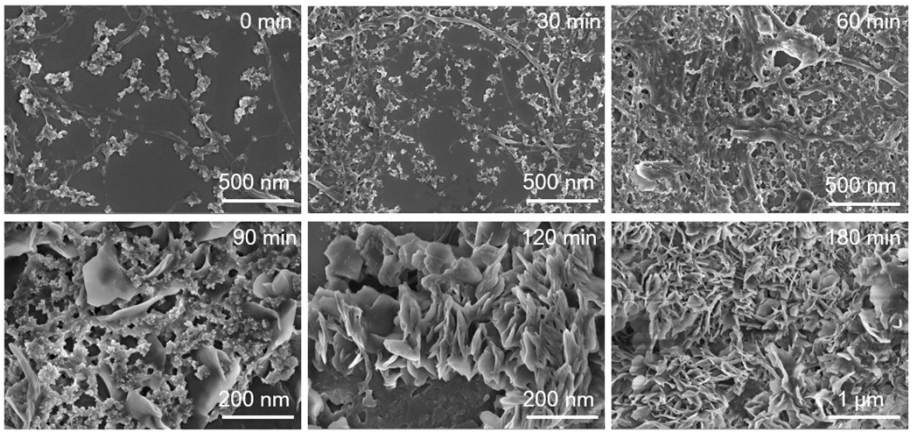


Fig. S18 Time-dependent SEM images to visualize the self-assembly process (0 ~ 180 min) of **DPAC-R-GLD** in H_2O/THF solution (f_w = 80%) at 298 K.

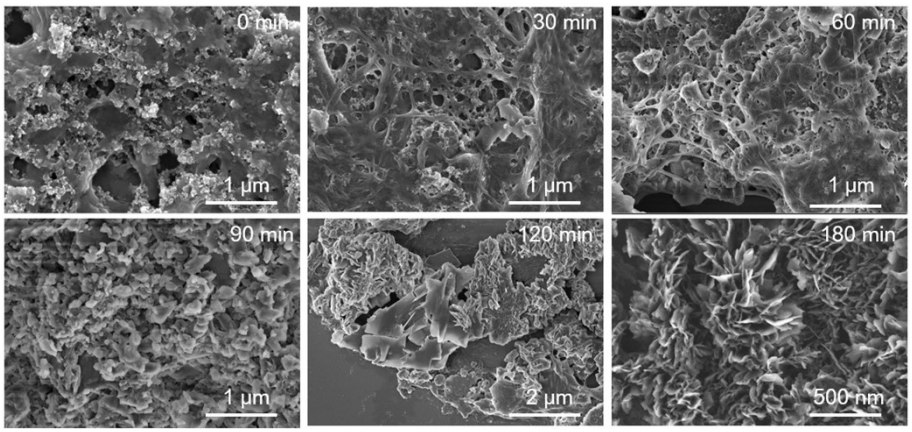


Fig. S19 Time-dependent SEM images to visualize the self-assembly process (0 ~ 180 min) of **DPAC-S-GLD** in H_2O/THF solution (f_w = 80%) at 298 K.

5. Characterization of ^{1}H NMR, ^{13}C NMR and HRMS spectra

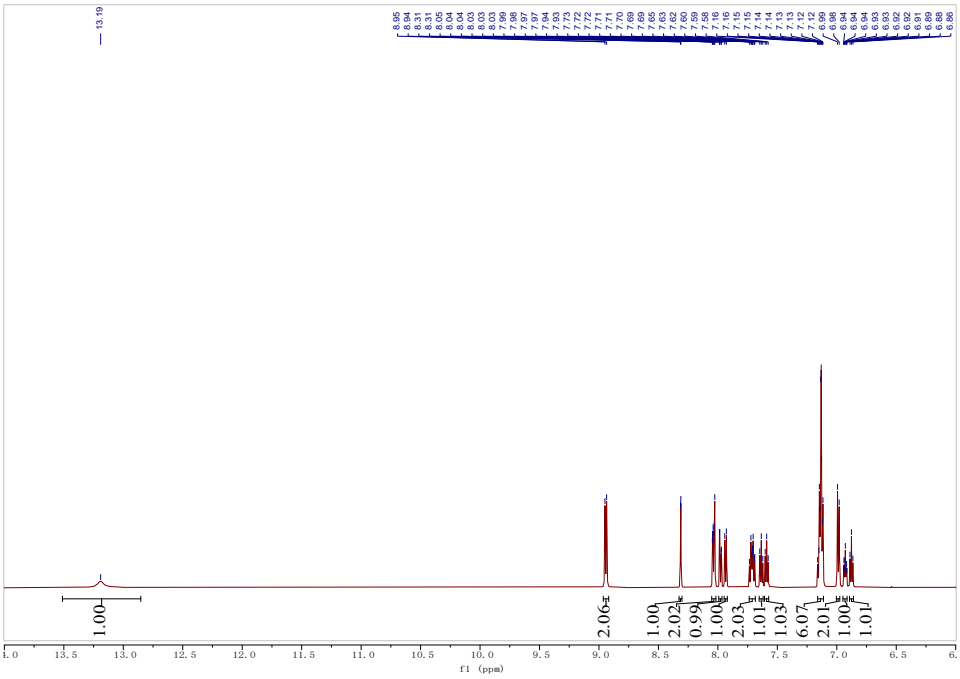


Fig. S20 ^{1}H NMR spectrum (600 MHz) of **DPAC-COOH** in DMSO-d_6.

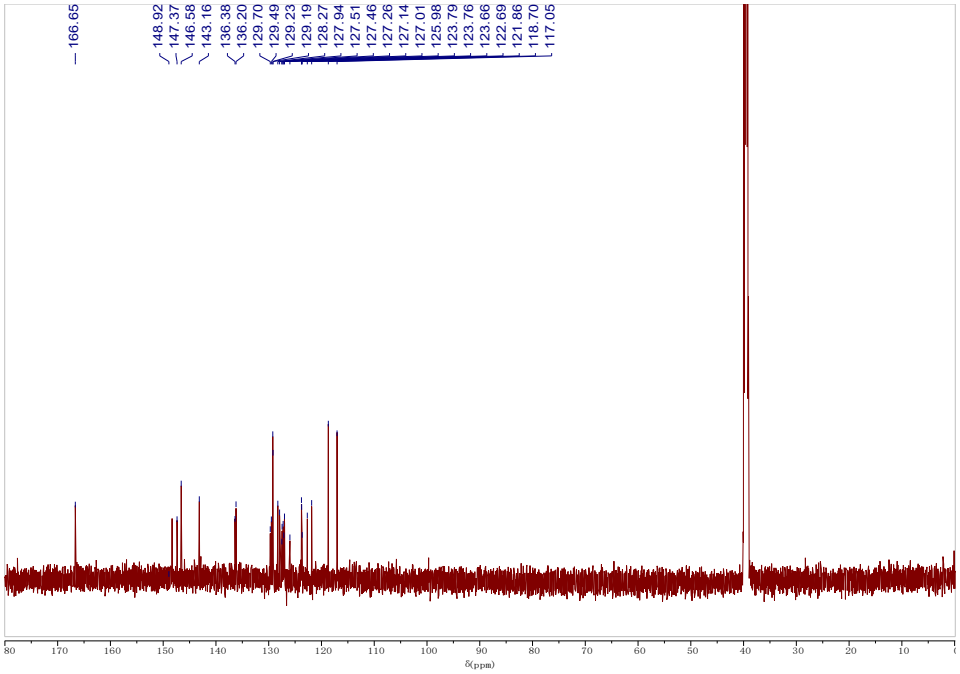


Fig. S21 ^{13}C NMR spectrum (151 MHz) of **DPAC-COOH** in DMSO-d_6.

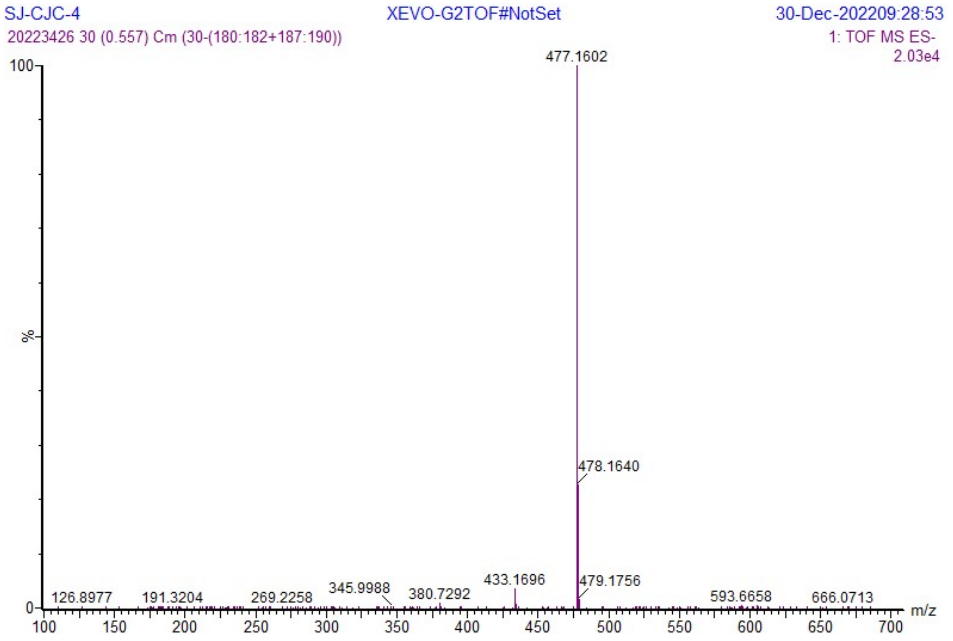


Fig. S22 HRMS (ESI) of **DPAC-COOH**.

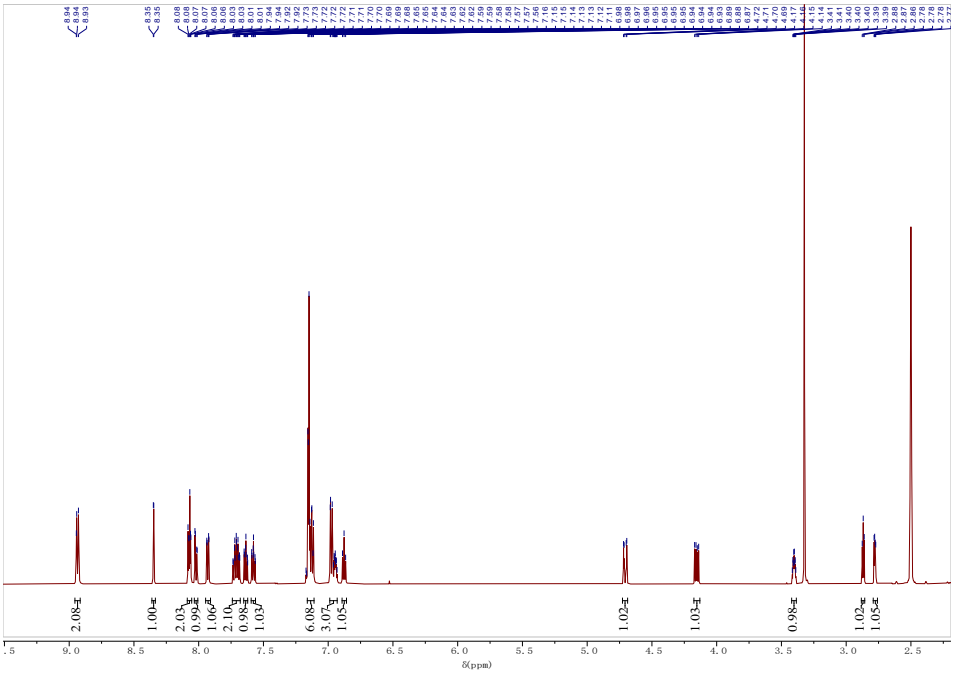


Fig. S23 ^{1}H NMR spectrum (600 MHz) of **DPAC-R-GLD** in DMSO-d_6.

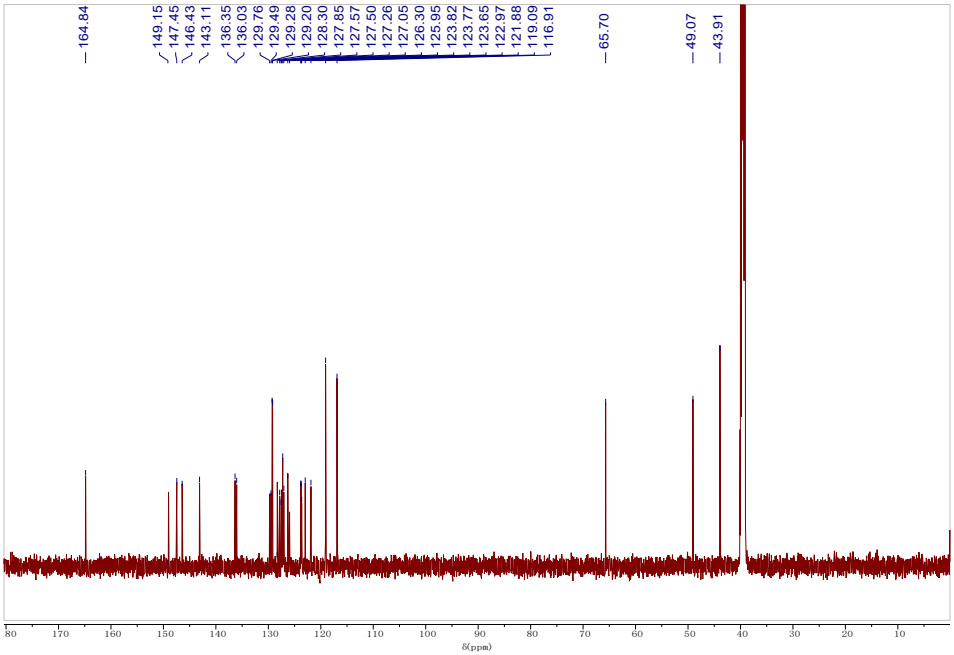


Fig. S24 ^{13}C NMR spectrum (151 MHz) of **DPAC-R-GLD** in DMSO-d_6.

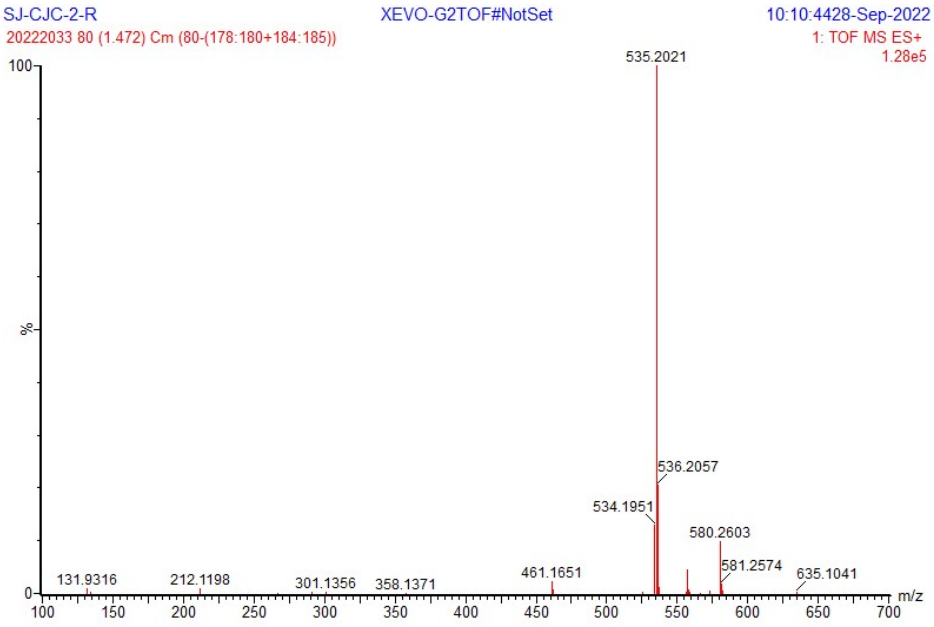


Fig. S25 HRMS (ESI) of **DPAC-R-GLD**.

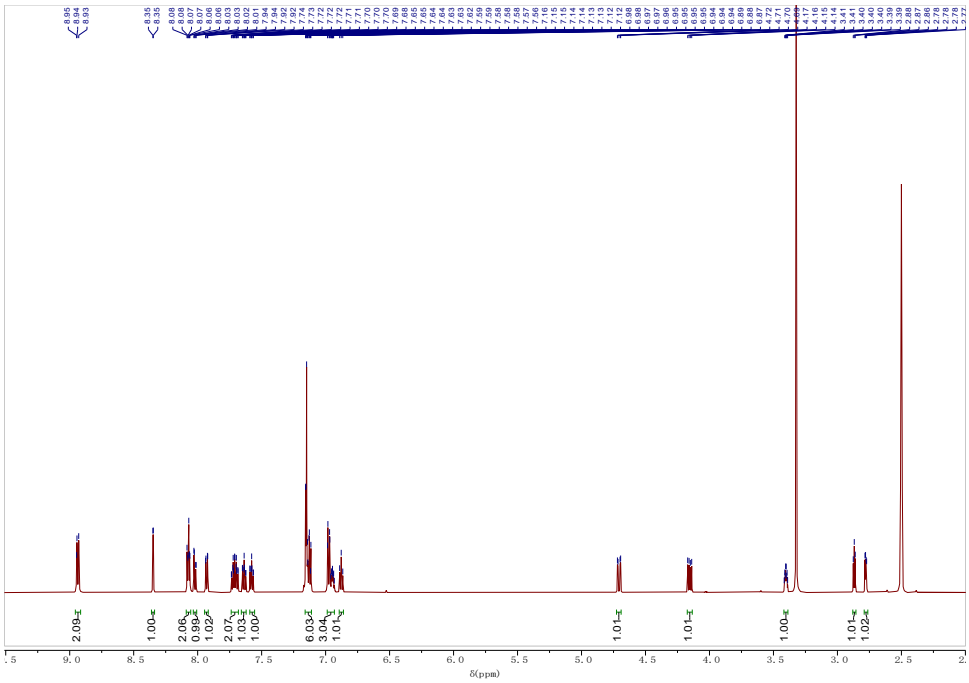


Fig. S26 ^{1}H NMR spectrum (600 MHz) of **DPAC-S-GLD** in DMSO-d_6.

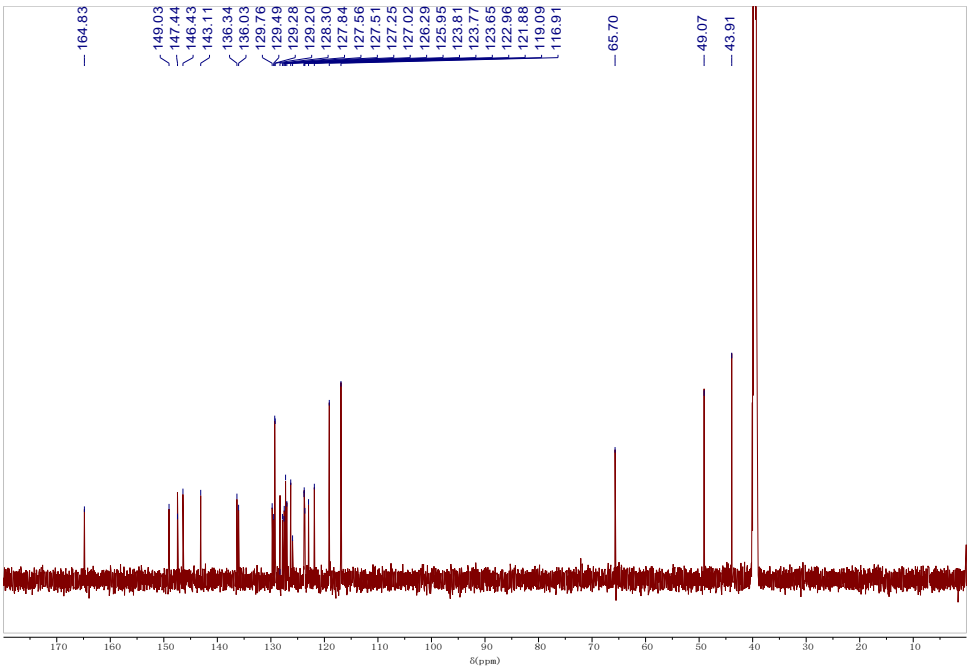


Fig. S27 ^{13}C NMR spectrum (151 MHz) of **DPAC-S-GLD** in DMSO-d_6.

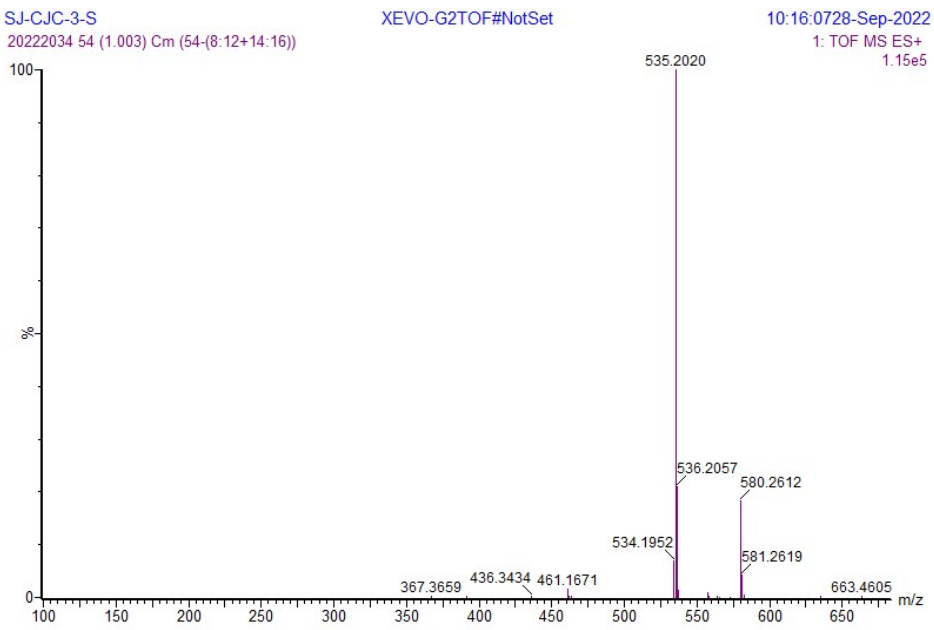


Fig. S28 HRMS (ESI) of **DPAC-S-GLD**.

6. References

[1] Y. Zhang, Y. Li, H. Wang, Z. Zhang, Y. Feng, Q. Tian, N. Li, J. Mei, J. Su, H. Tian, Measuring the Microphase Separation Scale of Polyurethanes with a Vibration-Induced Emission-Based Ratiometric "Fluorescent Ruler", *ACS Appl. Mater. Interfaces,* 2019, **11**, 39351-39358.