

## Electronic Supporting information (ESI) for

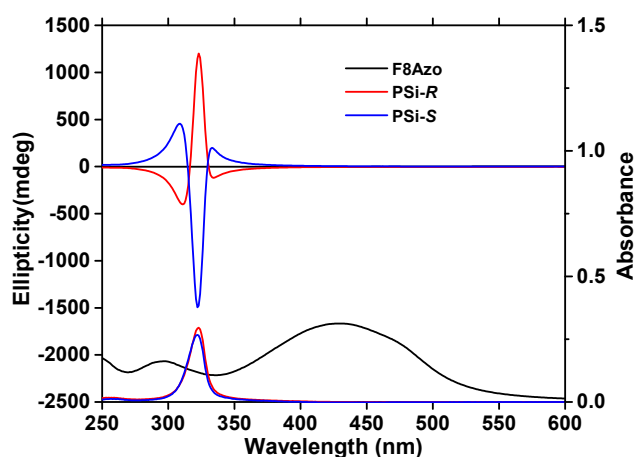
### Aggregation-induced chiroptical generation and photoinduced switching of achiral azobenzene-alt-fluorene copolymer endowed with left- and right-handed helical polysilanes

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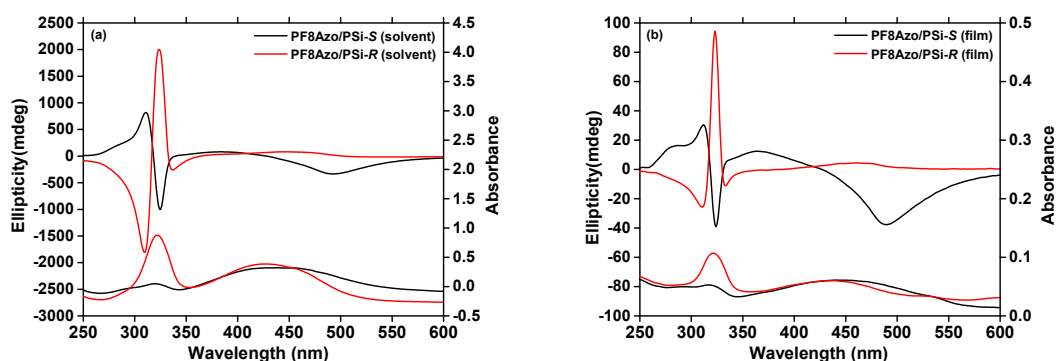
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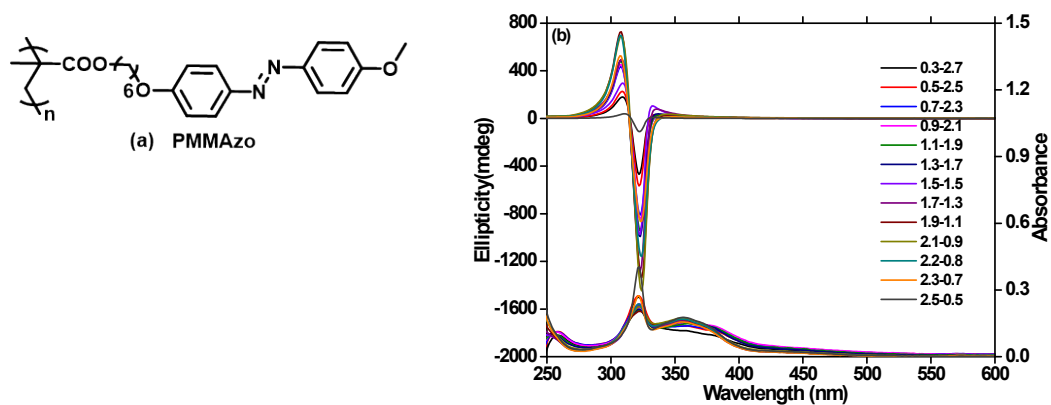
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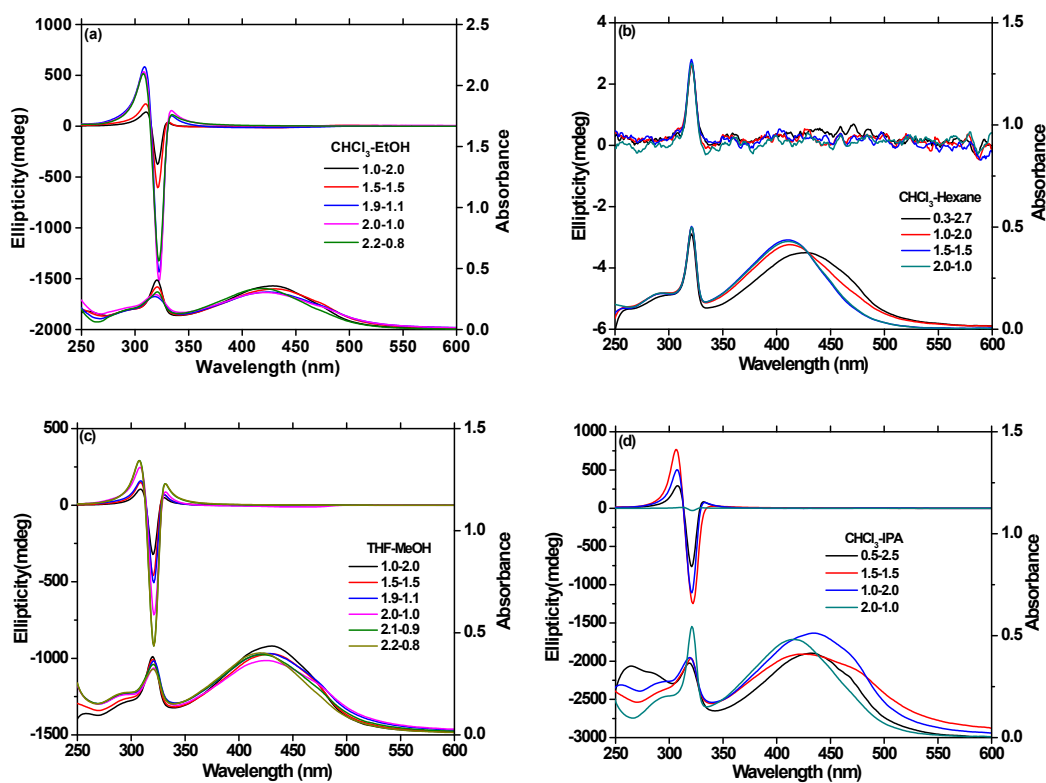
**Fig. S1.** CD and UV-vis spectra of PF8Azo and PSI-S/-R homo-aggregates in  $\text{CHCl}_3$ -MeOH cosolvent (2.0/1.0, (v/v)).  $[\text{PSI-S/-R}]_0 = [\text{PF8Azo}]_0 = 1.0 \times 10^{-5}$  M.



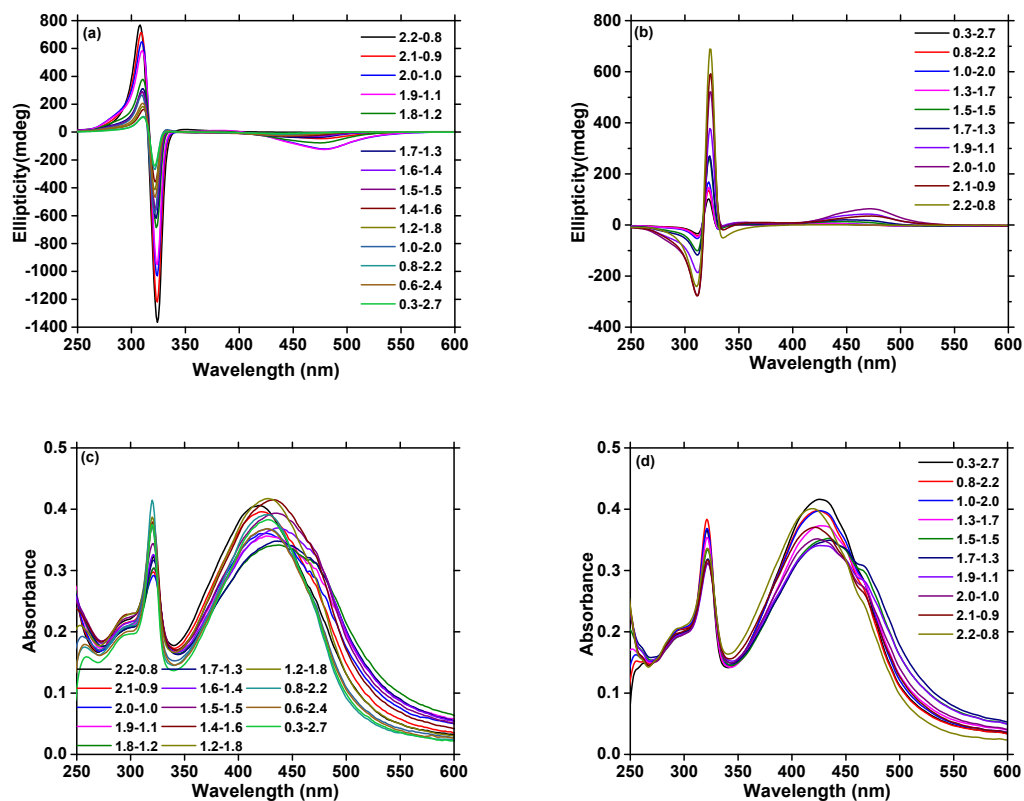
**Fig. S2.** (a) CD and UV-vis spectra of PF8Azo/PSI-S (black line) and PF8Azo/PSI-R (red line) hetero-aggregates in cosolvent and (b) CD and UV-vis spectra of the dried hetero-aggregate in grease onto quartz substrate. The aggregates are generated that  $[\text{PSI-S/-R}]_0 = [\text{PF8Azo}]_0 = 2.0 \times 10^{-5}$  M in chloroform-methanol (2.0/1.0, (v/v)) cosolvent.



**Fig. S3.** (a) Chemical structure of PMMAzo ( $M_n = 14,400$  Da,  $M_w/M_n = 1.14$ ,  $DP_n = 36$ ); (b) Changes in CD and UV-vis spectra of hetero-aggregates of PMMAzo-PSi-5 that with different volume ratio of  $\text{CHCl}_3$ -MeOH. ( $[\text{PSi-S}]_0 = [\text{PMMAzo}]_0 = 1.0 \times 10^{-5}$  M).



**Fig. S4.** CD and UV-vis spectra of hetero-aggregates including PSi-S and PF8Azo with a 1-to-1 molar ratio produced in different cosolvents with different volume ratio. [(a)chloroform-ethanol; (b)chloroform-hexane; (c)tetrahydrofuran-methanol; (d)chloroform-isopropanol. ] Their repeating units are  $[\text{PSi-S/-R}]_0 = [\text{PF8Azo}]_0 = 1.0 \times 10^{-5}$  M.



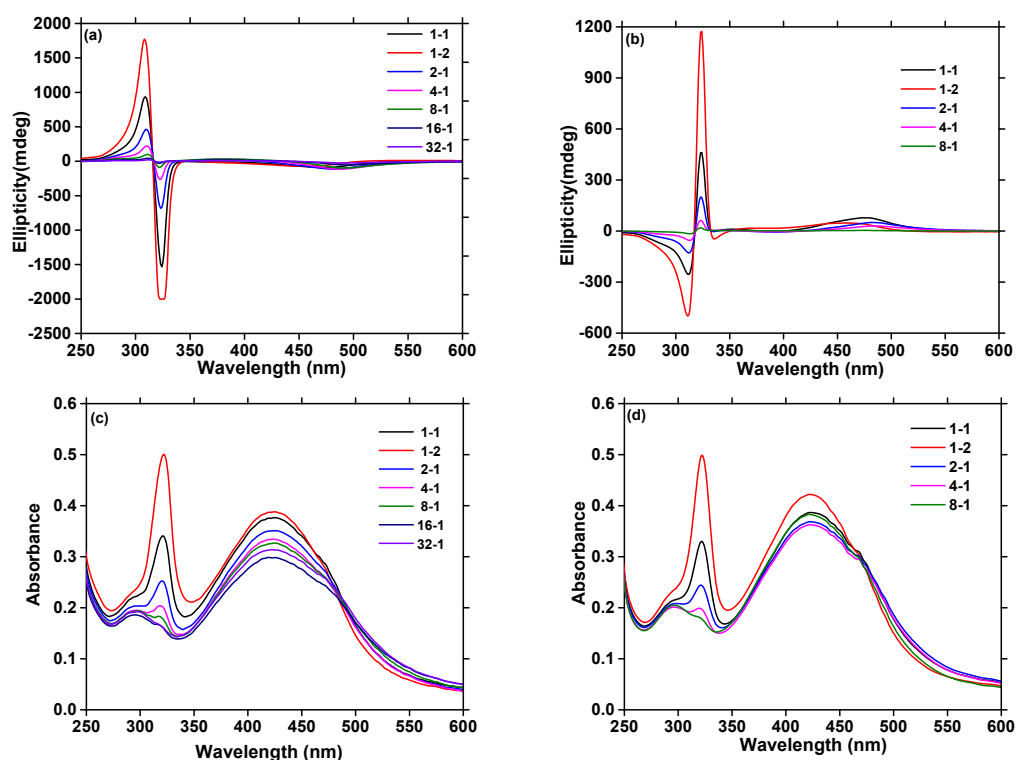
**Fig. S5.** Changes in CD spectra of hetero-aggregates of (a)PF8Azo/PSi-S and (b) PF8Azo/PSi-R that with different volume ratio of  $\text{CHCl}_3$ -MeOH. UV-vis spectra (c)and (d) show corresponding UV changes respectively. ( $[\text{PSi-S/-R}]_0 = [\text{PF8Azo}]_0 = 1.0 \times 10^{-5} \text{ M}$ ).

**Table S1.** Changes in particle size of PSi-S homo-aggregates with different volume ratio of  $\text{CHCl}_3$ -MeOH. ( $[\text{PSi-S}]_0 = 1.0 \times 10^{-5} \text{ M}$ ).

$\text{CHCl}_3$ -MeOH	Eff.Diam.(nm)	PDI
0.3-2.7	678.3	0.21
0.5-2.5	617.8	0.18
0.8-2.2	562.7	0.18
1.0-2.0	535.3	0.20
1.3-1.7	509.2	0.13
1.5-1.5	492.0	0.19
1.7-1.3	473.4	0.10
1.9-1.1	474.3	0.16
2.0-1.0	484.2	0.12
2.1-0.9	386.4	0.14
2.2-0.8	319.6	0.09
2.3-0.7	310.8	0.09
2.4-0.6	184.7	0.13

**Table S2.** Changes in particle size of PF8Azo homo-aggregates with different volume ratio of CHCl<sub>3</sub>-MeOH. ([PF8Azo]<sub>0</sub> = 1.0×10<sup>-5</sup> M).

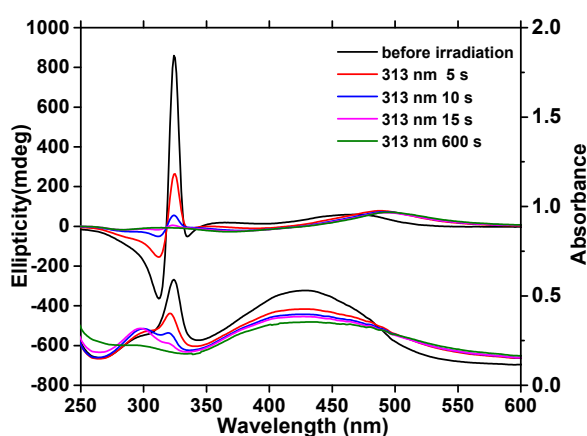
CHCl <sub>3</sub> -MeOH	Eff. Diam.(nm)	PDI
0.3-2.7	1776.8	0.39
0.5-2.5	969.8	0.32
0.8-2.2	794.7	0.26
1.0-2.0	685.3	0.24
1.3-1.7	629.4	0.19
1.5-1.5	471.7	0.16
1.7-1.3	314.4	0.07
1.9-1.1	284.7	0.12
2.0-1.0	263.8	0.08
2.1-0.9	250.7	0.08
2.2-0.8	318.7	0.14
2.3-0.7	230.6	0.10
2.4-0.6	225.2	0.12



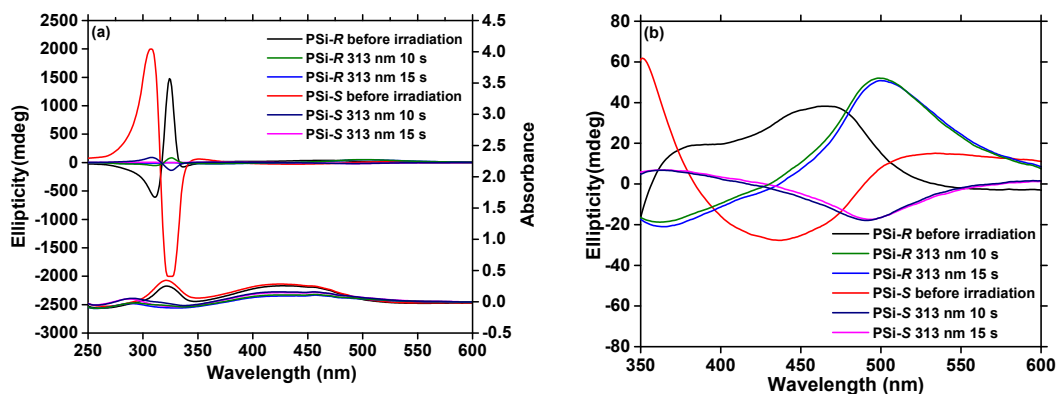
**Fig. S6.** Changes in CD spectra of hetero-aggregates of (a)PF8Azo/Psi-S and (b)PF8Azo/Psi-R that with different molar ratio of PF8Azo-to-Psi-S/-R ([PF8Azo]<sub>0</sub> = 1.0×10<sup>-5</sup> M). UV-vis spectra (c)and (d) show corresponding UV changes respectively. The volume ratio of CHCl<sub>3</sub>-MeOH = 2-1.

**Table S3.** Changes in  $g_{CD}$  values at 320 nm and 475 nm of the hetero-aggregates before and after the irradiation of 313-nm light. The hetero-aggregates were prepared under the condition that the volume ratio ( $\text{CHCl}_3$ -MeOH) was 2-to-1 and the molar ratio was 1-to-1 ( $[\text{PSi-S/-R}]_0 = [\text{PF8Azo}]_0 = 1.0 \times 10^{-5} \text{ M}$ ).

Hetero-aggregate	$g_{CD}/10^{-3}$	Before irradiation	313 nm 5 s	313 nm 10 s	313 nm 15 s
PF8Azo/PSi-S	at 320 nm	-83.27	5.348	6.878	7.253
	at 475 nm	-12.34	-21.73	-21.14	-20.40
PF8Azo/PSi-R	at 320 nm	23.61	9.706	4.613	0.6477
	at 475 nm	6.492	9.184	8.625	8.071



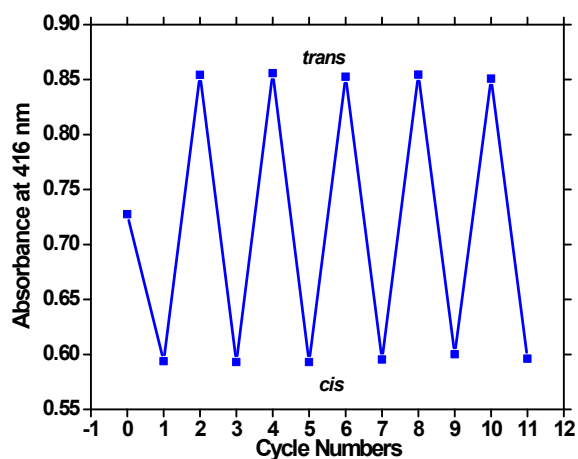
**Fig. S7.** Changes in CD and UV-vis spectra of PF8Azo/PSi-R hetero-aggregates before and after the irradiation of 313-nm light. The hetero-aggregates were prepared under the condition that the volume ratio ( $\text{CHCl}_3$ -MeOH) was 2-to-1 and the molar ratio was 1-to-1 ( $[\text{PSi-R}]_0 = [\text{PF8Azo}]_0 = 1.0 \times 10^{-5} \text{ M}$ ).



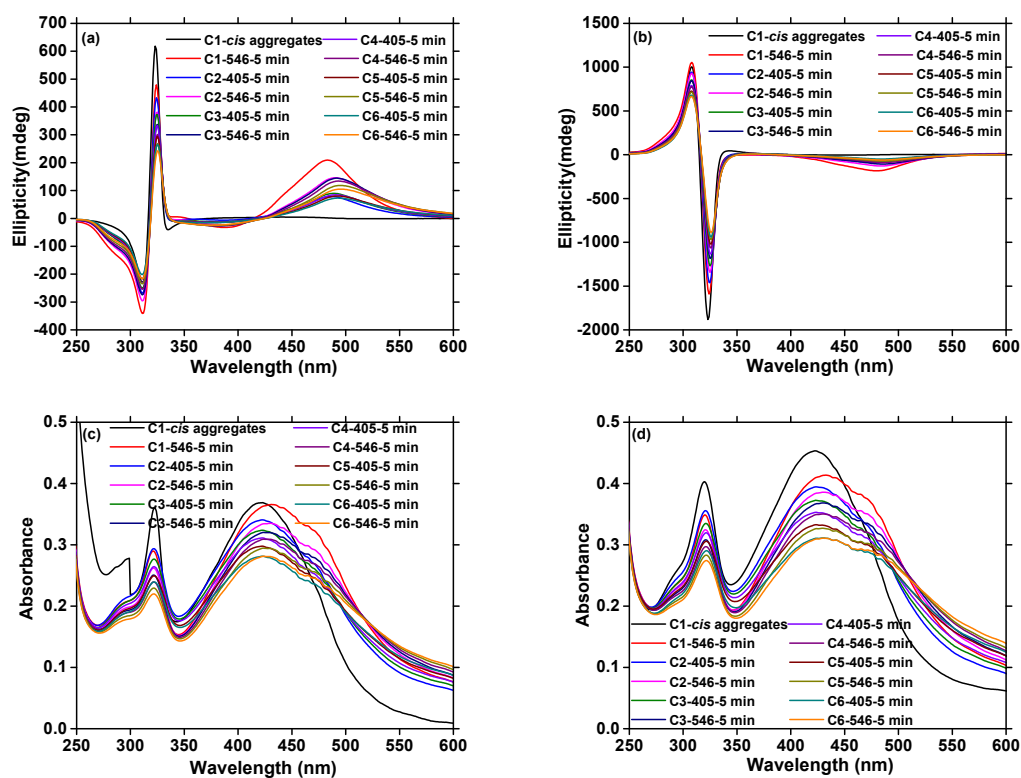
**Fig. S8.** (a) Changes in CD and UV-vis spectra of the PF8Azo/PSi-R and PF8Azo/PSi-S hetero-aggregates before and after the irradiation of 313-nm light. (b) is magnified part of (a). The hetero-aggregates were prepared under the condition that the volume ratio ( $\text{CHCl}_3$ -MeOH) was 2.1-to-0.9 and the molar ratio was 1-to-1 ( $[\text{PSi-S/-R}]_0 = [\text{PF8Azo}]_0 = 1.0 \times 10^{-5} \text{ M}$ ).

**Table S4.** Effective particle size of PSi-S homo-aggregates variation with time. ( $[\text{PSi-S}]_0 = 1.0 \times 10^{-5} \text{ M}$ ,  $\text{CHCl}_3\text{-MeOH} = 1\text{-}2$ )

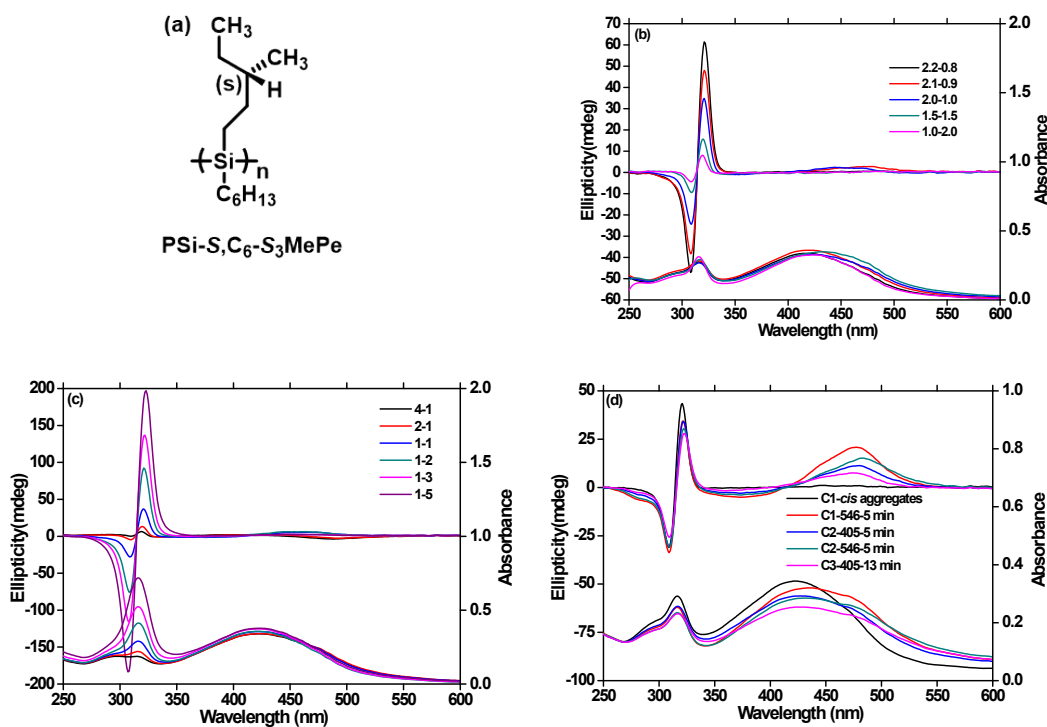
Time(min)	Eff. Diam.(nm)	PDI
1	421.1	0.16
2	467.3	0.14
3	524.6	0.14
4	535.3	0.20
5	597.6	0.19



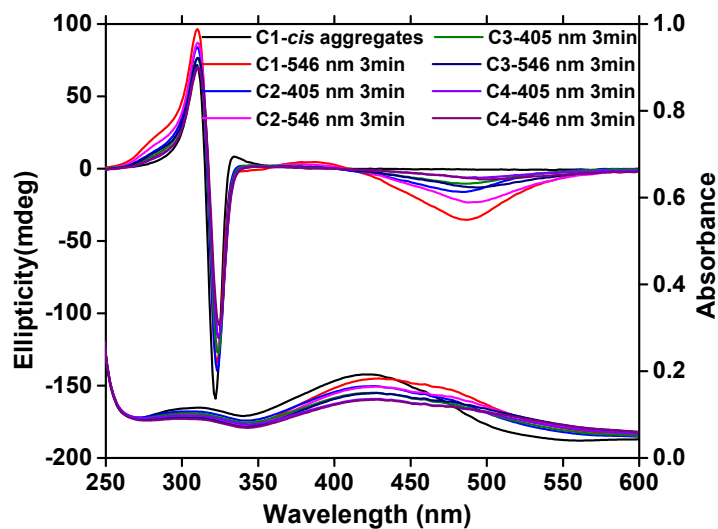
**Fig. S9.** Reversible photo-isomerization of non-aggregate PF8Azo dissolved in  $\text{CHCl}_3$  upon alternating irradiation with 405-nm and 546-nm light. Irradiation time:15 min,  $[\text{PF8Azo}]_0 = 1.0 \times 10^{-5} \text{ M}$ .



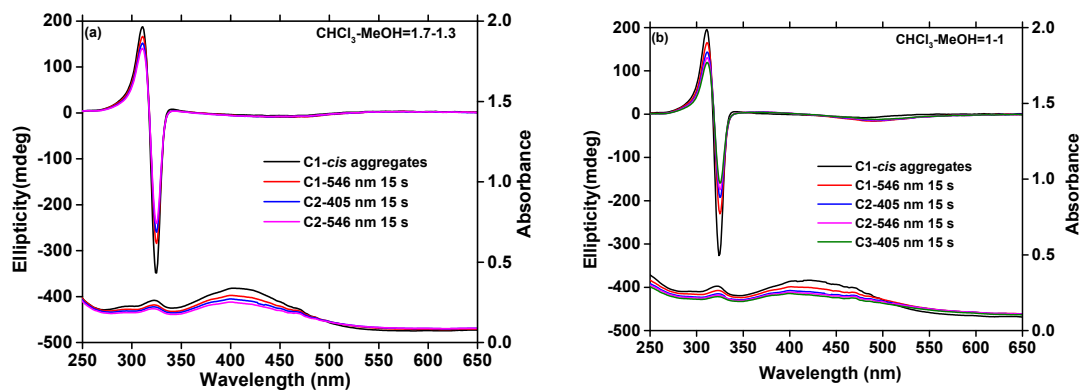
**Fig. S10.** Changes in CD spectra of hetero-aggregates of (a) PF8Azo/PSi-R and (b) PF8Azo/PSi-S upon alternating photoirradiation cycles with 405-nm and 546-nm light in  $\text{CHCl}_3\text{-MeOH}$  cosolvent (2.0/1.0, (v/v)). UV-vis spectra (c) and (d) show corresponding UV changes respectively. ( $[\text{PSi-S/R}]_0 = [\text{PF8Azo}]_0 = 1.0 \times 10^{-5} \text{ M}$ ). A  $\text{CHCl}_3$  solution of PF8Azo was irradiated for 15 min with 405-nm light, then aggregate with PSi-S/-R in  $\text{CHCl}_3\text{-MeOH}$  cosolvent to obtain the *cis* aggregates.



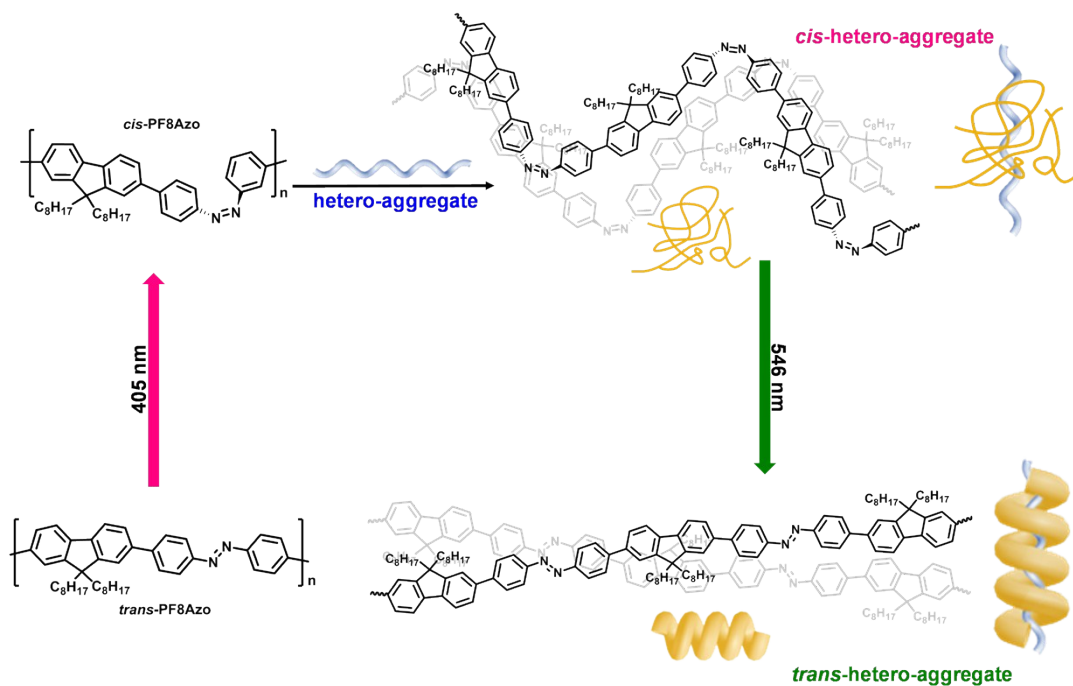
**Fig. S11.** (a) Chemical structure of  $C_6-S_3MePe$ . Changes in CD and UV-vis spectra of hetero-aggregates of (b) PF8Azo/ $C_6-S_3MePe$  that with different volume ratio of  $CHCl_3$ -MeOH ( $[C_6-S_3MePe]_0 = [PF8Azo]_0 = 1.0 \times 10^{-5}$  M), (c) PF8Azo/ $C_6-S_3MePe$  with different molar ratio of PF8Azo-to- $C_6-S_3MePe$  ( $[PF8Azo]_0 = 1.0 \times 10^{-5}$  M). (d) Changes in CD and UV-vis spectra of reversible photoisomerization of PF8Azo/ $C_6-S_3MePe$  hetero-aggregates upon alternating 405-nm and 546-nm light. The  $M_n$  values of  $C_6-S_3MePe$  and PF8Azo are 32,100 Da and 23,900 Da respectively.



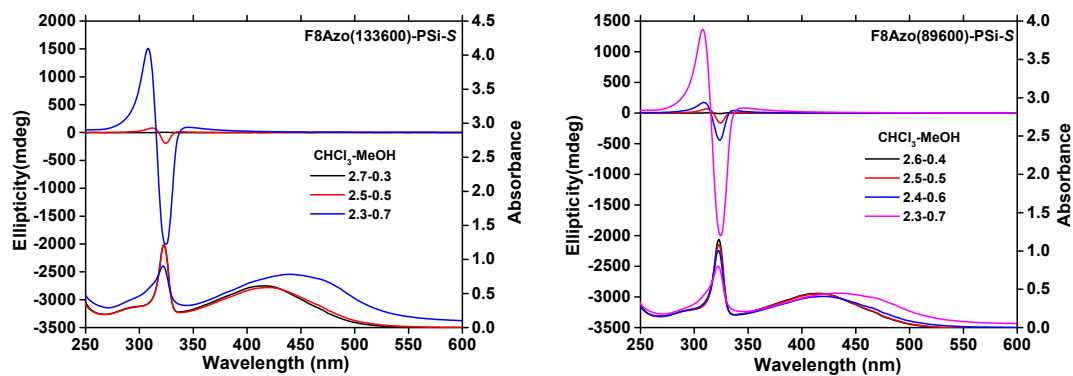
**Fig. S12.** Changes in CD and UV-vis spectra of PF8Azo-Psi-S hetero-aggregates upon alternating photoirradiation cycles with 405-nm and 546-nm light in  $CHCl_3$ -MeOH cosolvent (2.0/1.0, (v/v)). The molar ratio of PF8Azo-to-Psi-S is 4-to-1. ( $[PF8Azo]_0 = 0.5 \times 10^{-5}$  M). A  $CHCl_3$  solution of PF8Azo was irradiated for 15 min with 405-nm light, then aggregate with Psi-S in  $CHCl_3$ -MeOH cosolvent to obtain the *cis* aggregates.



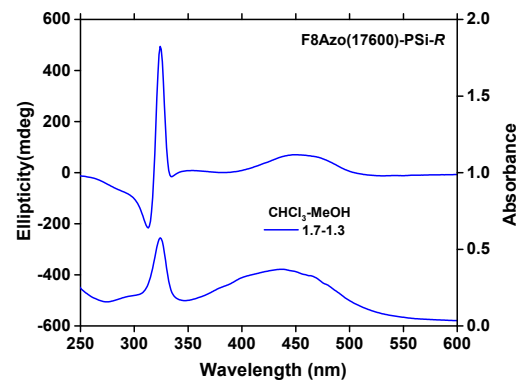
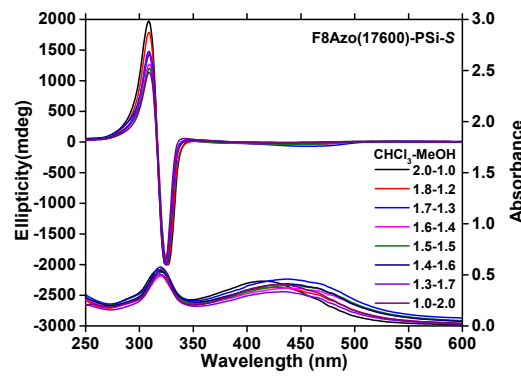
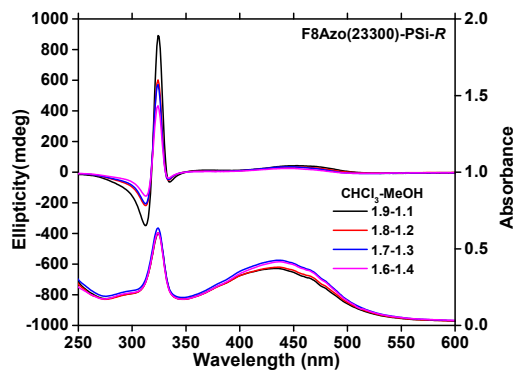
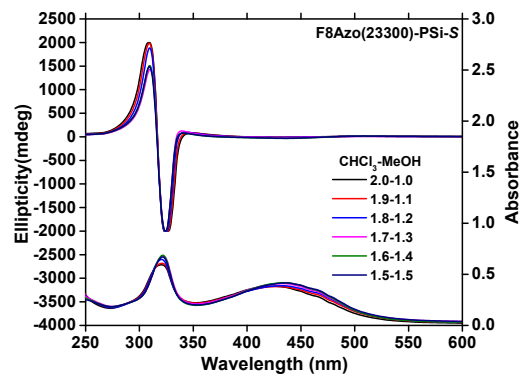
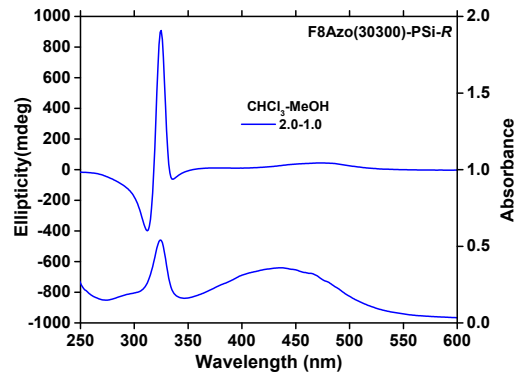
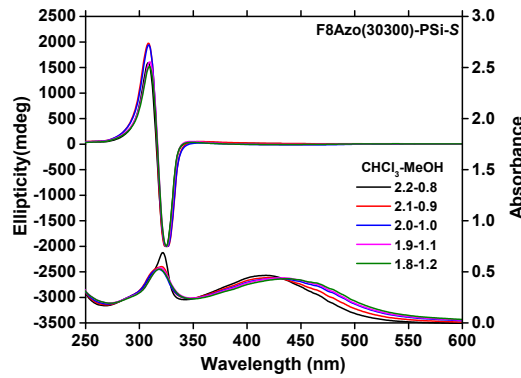
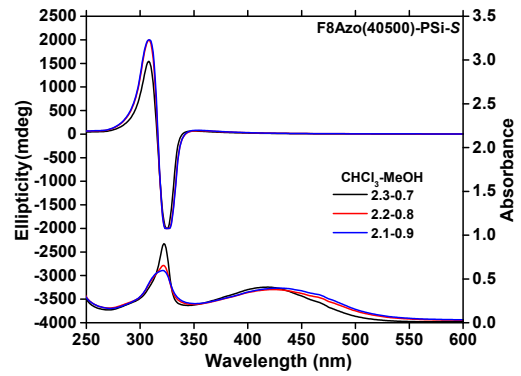
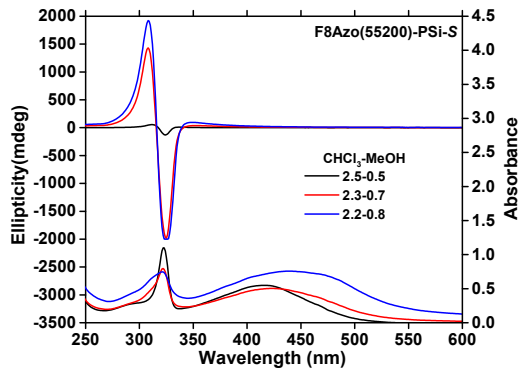
**Fig. S13.** Changes in CD and UV-vis spectra of PF8Azo/PSi-S hetero-aggregates upon alternating photoirradiation cycles with 405-nm and 546-nm light in  $\text{CHCl}_3$ -MeOH cosolvent [(a)1.7/1.3, (v/v) ; (b)1/1, (v/v)]. The molar ratio of PF8Azo-to-PSi-S is 1-to-1.  $[\text{PF8Azo}]_0 = 1.0 \times 10^{-5} \text{ M}$ ,  $M_n(\text{PF8Azo}) = 7,300 \text{ Da}$ . A  $\text{CHCl}_3$  solution of PF8Azo was irradiated for 15 min with 405-nm light, then aggregate with PSi-S in  $\text{CHCl}_3$ -MeOH cosolvent to obtain the *cis* aggregates.

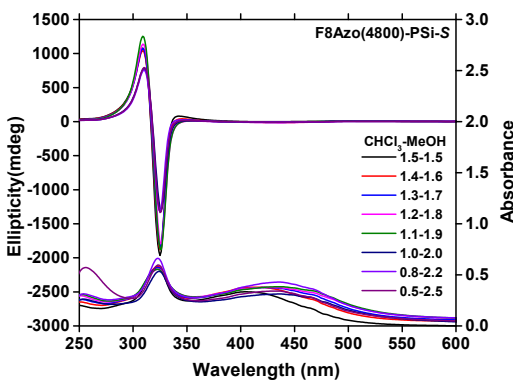
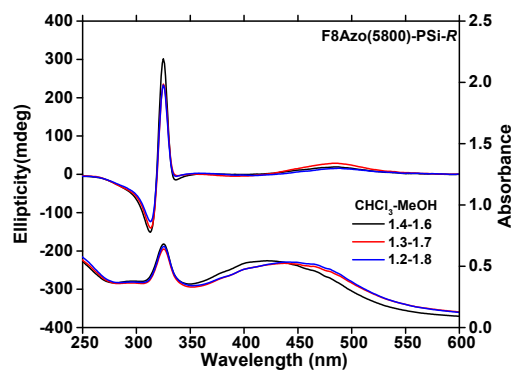
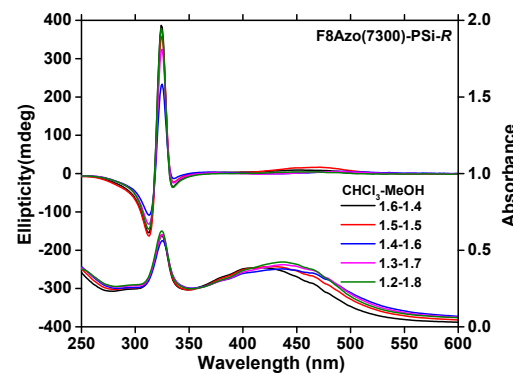
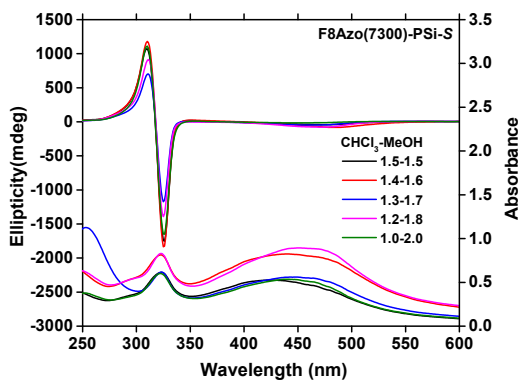
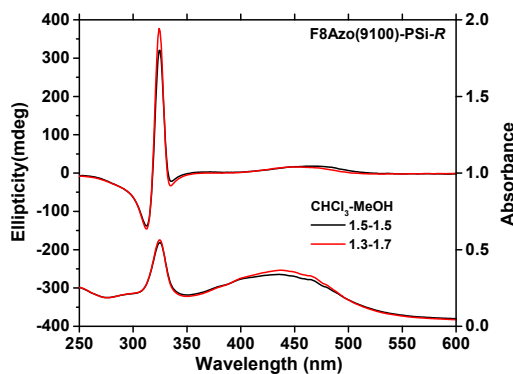
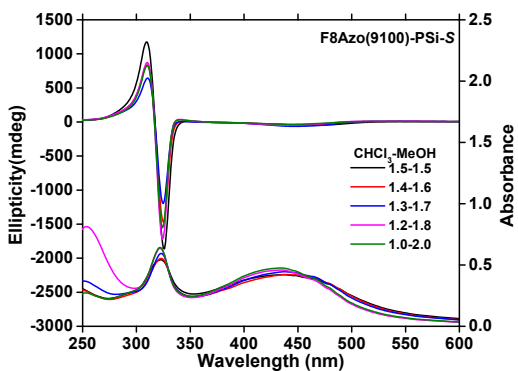
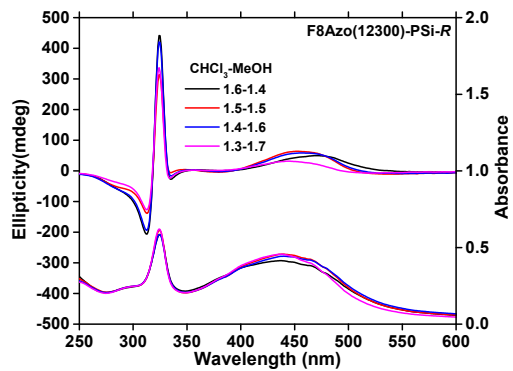
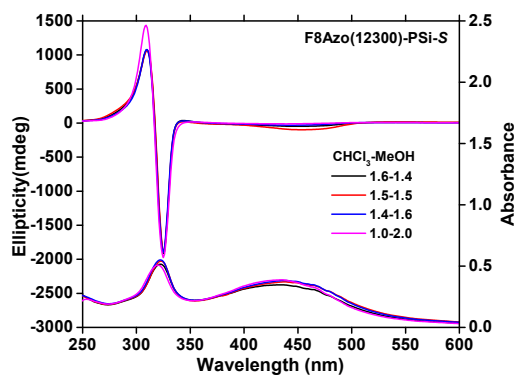


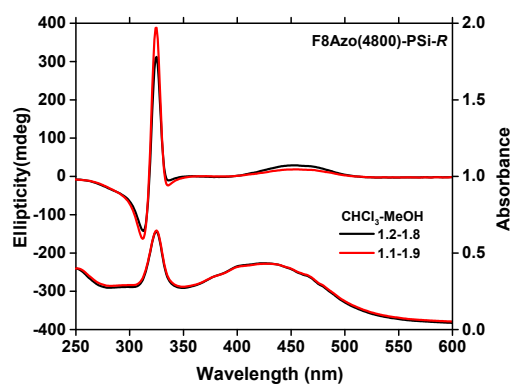
**Scheme S1.** Proposed mechanism for the enhancement of  $g_{\text{CD}}$  upon 1st photoirradiation at 546 nm.











**Fig. S14.** Changes in CD and UV-vis spectra of PSi-S/-R hetero-aggregates with PF8Azo which has different  $M_{n,GPC}$ . The hetero-aggregates were prepared under the condition that the molar ratio was 1-to-1 ( $[PSi-S/-R]_0 = [PF8Azo]_0 = 1.0 \times 10^{-5}$  M) in  $CHCl_3$ -MeOH cosolvent that with different volume ratio.

**Table S5.** Molecular weight characteristics and number-average degree of polymerization of PF8Azo that applied for exploring molecular weight effects.

Fraction	$M_{n,GPC}$ (g/mol)	$M_w/M_n$	$DP_n$
1	133,600	1.53	234
2	89,600	1.63	157
3	55,200	1.69	97
4	40,500	1.27	71
5	30,300	1.68	53
6	23,300	1.18	41
7	17,600	1.42	31
8	12,300	1.17	22
9	9,100	1.06	16
10	7,300	1.03	13
11	5,800	1.05	10
12	4,800	1.02	8