Supporting Information for

Synthesis of Monodisperse Aromatic Azo Oligomers toward a New Insight into the Isomerization of π-Conjugated Azo systems

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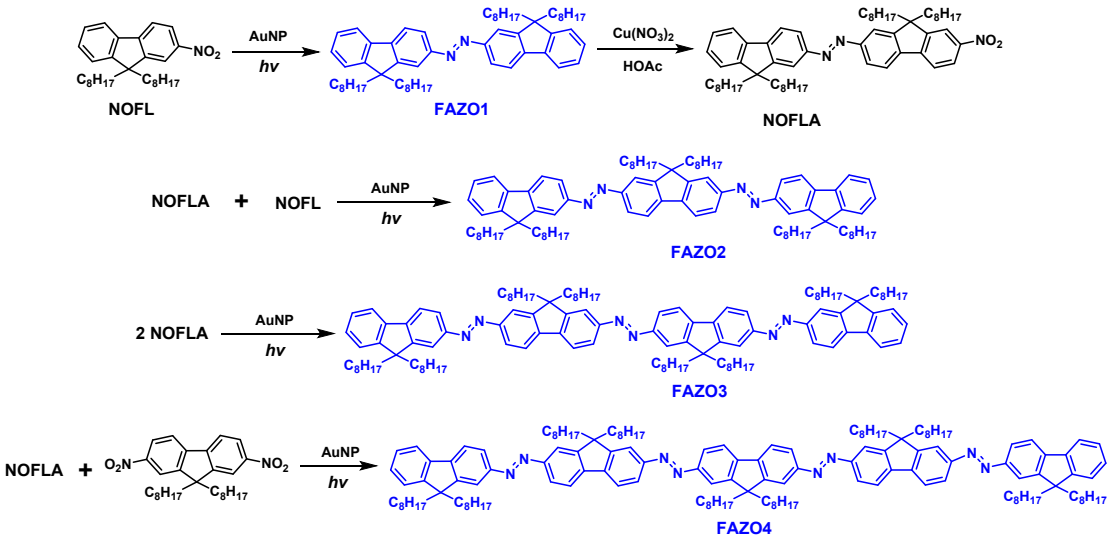

Scheme 1. Synthetic routes of aromatic Azo derivatives (FAZOn, n =1, 2, 3 and 4).

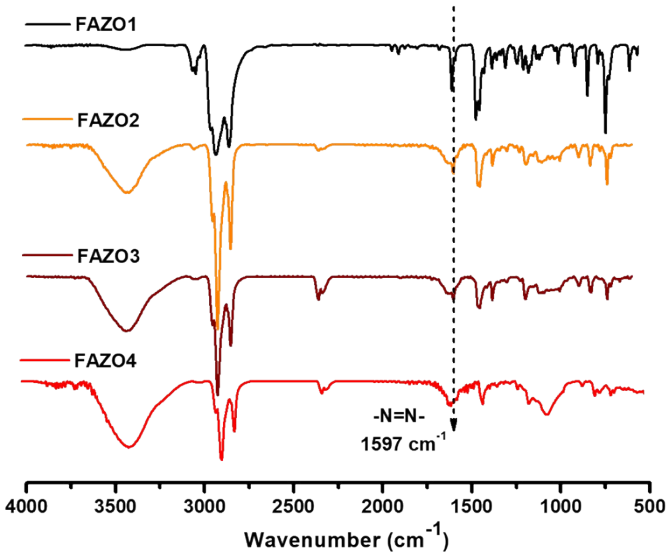

Fig. S1. FT-IR spectra of FAZOn (n = 1, 2, 3 and 4).

Table S1. Summary of Azo-oligomers FAZOn (n = 1, 2, 3 and 4).

Entry	$M_{n,GPC}$（g/mol）	$M_{n,th}$（g/mol）
FAZO1	990	806.65
FAZO2	1640	1222.97
FAZO3	2370	1639.29
FAZO4	3050	2055.61

The first-order rate constant k_{eS} of *trans*-to-*cis* photoisomerization was determined by the Formula S1[1,2]:

$$Ln[(A_\infty-A_t)/(A_\infty-A_0)] = -k_{eS}t \qquad \text{Formula S1}$$

Where A_∞, A_t, and A_0 are absorbance corresponded to the π-π* transition of *trans* isomers at infinite time, time t and time zero with irradiation of different wavelength light (404 nm, and 435 nm) at room temperature, respectively.

The first-order rate constant k_{HS} of *cis*-to-*trans* recovery was determined by the Formula S2[1,2]:

$$Ln[(A_\infty-A_t)/(A_\infty-A_0)] = -k_{HS}t \qquad \text{Formula S2}$$

Where A_∞, A_t, and A_0 are absorbance corresponded to the π-π* transition of trans isomers of azobenzene at infinite time, time t and time zero with irradiation of 546 nm light at room temperature.

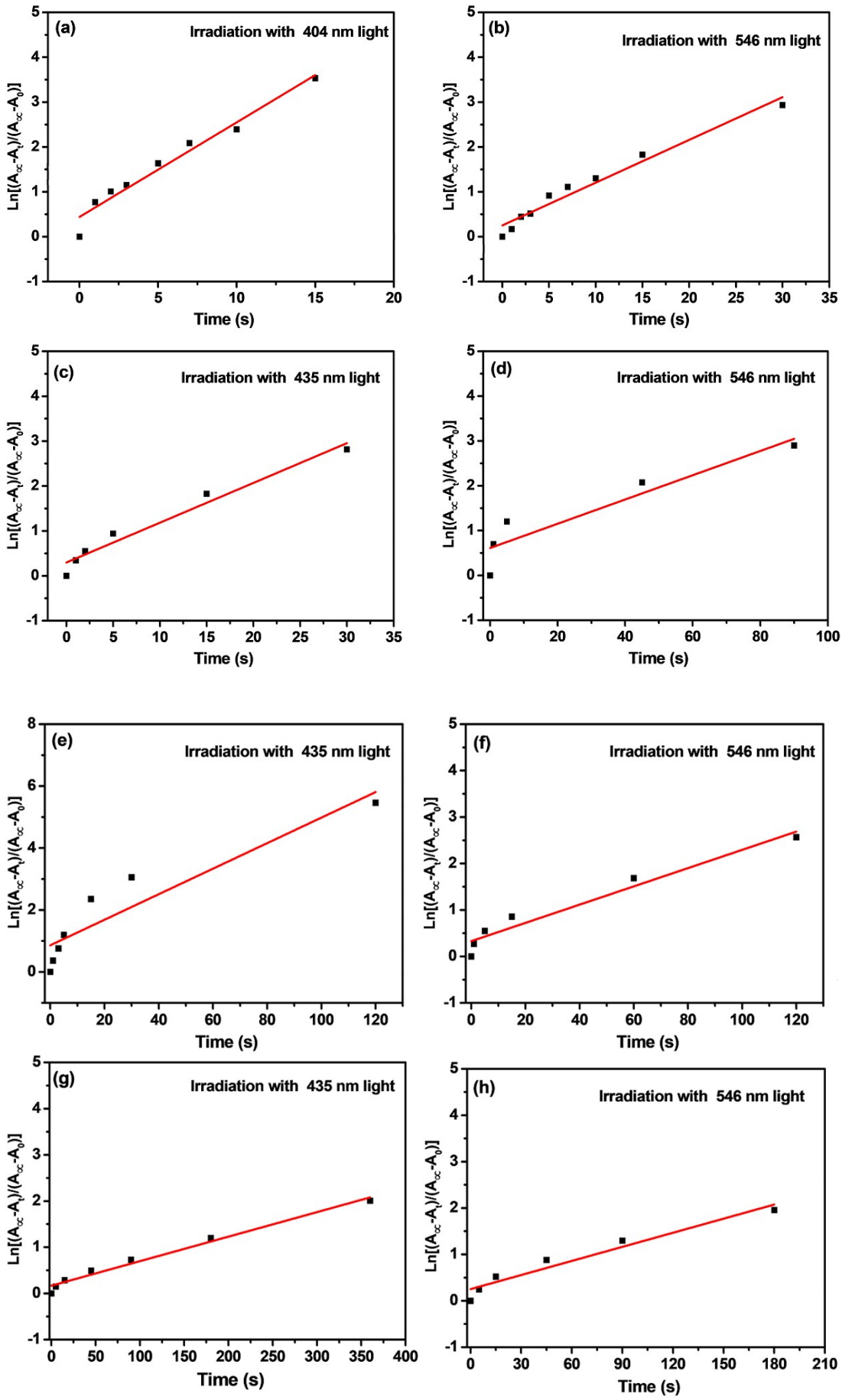
(a)
Irradiation with 404 nm light
(b)
Irradiation with 546 nm light
(c)
Irradiation with 435 nm light
(d)
Irradiation with 546 nm light
(e)
Irradiation with 435 nm light
(f)
Irradiation with 546 nm light
(g)
Irradiation with 435 nm light
(h)
Irradiation with 546 nm light
Ln[(A∞-At)/(A∞-A0)]
Time (s)

Fig. S2 First-order kinetics for the photoisomerization of of FAZO1 (a and b), FAZO2 (c and d), FAZO3 (e and f) and FAZO4 (g and h) in DCE under different times with 404 nm, 435 nm and 546 nm light.

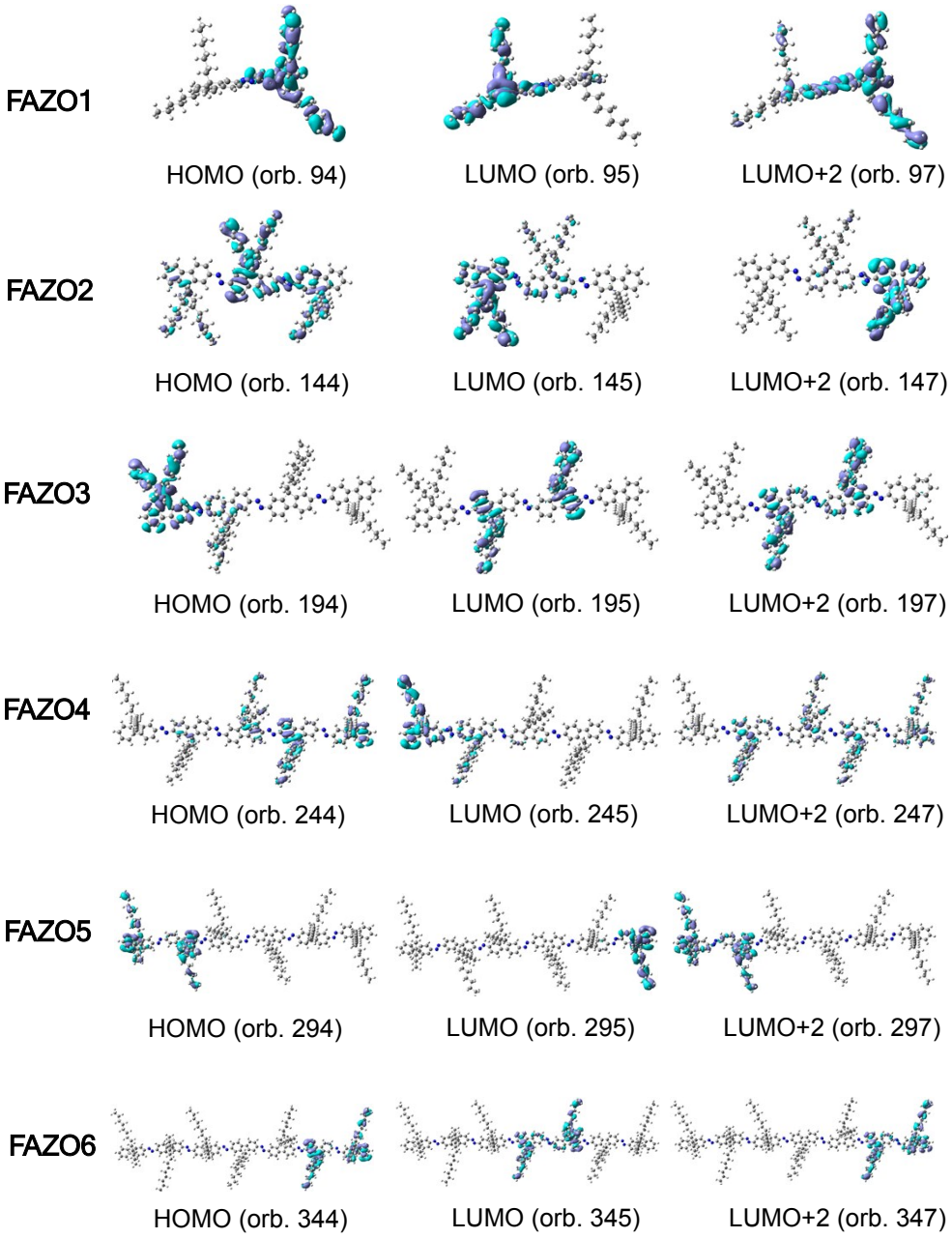

Fig S3. The graphical representation for molecular orbitals of FAZOn (n = 1, 2, 3, 4, 5, and 6).

Table S2 Main Calculated Optical Transitions for FAZOn (n = 1, 2, 3, 4, 5, and 6)

Orbital Excitations	Character	Calcd/nm	f^a
FAZO1			
HOMO→LUMO	π→π*	345	1.7154
HOMO→LUMO+2	π→π*	225	0.3852
FAZO2			
HOMO→LUMO	π→π*	378	3.0726
HOMO→LUMO+2	π→π*	228	0.1127
FAZO3			
HOMO→LUMO	π→π*	394	4.3887
HOMO→LUMO+2	π→π*	312	0.2968
FAZO4			
HOMO→LUMO	π→π*	403	5.7174
HOMO→LUMO+2	π→π*	333	0.4128
FAZO5			
HOMO→LUMO	π→π*	408	7.0233
HOMO→LUMO+2	π→π*	349	0.5506
FAZO6			
HOMO→LUMO	π→π*	412	8.3205
HOMO→LUMO+2	π→π*	361	0.6688

1. T. García, L. Larios-López, R. J. Rodríguez-González, G. Martínez-Ponce, C. Solano and D. Navarro-Rodríguez, *Polymer*, 2012, **53**, 2049-2061.
2. X. Jiang, J. Lu, F. Zhou, Z. Zhang, X. Pan, W. Zhang, Y. Wang, N. Zhou and X. Zhu, *Polym. Chem.*, 2016, **7**, 2645-2651