Supporting Information

Synthesis, one/two-photon optical and electrochemical properties, and photopolymerization-sensitizing effect of anthracene-based dyes: influence of the donor groups

Tanlong Xue,[ac] Di Zhao,[a] Tingting Hao,[a] Xiuyan Li,[b] Tao Wang *[a] and Jun Nie [ac]

[a] *State Key Laboratory of Chemical Resource Engineering, College of Science, Beijing University of Chemical Technology, Beijing 100029, China*

[b] *College of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China.*

[c] *College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.*

**Corresponding E-mail address: wangtwj2000@163.com*

Content

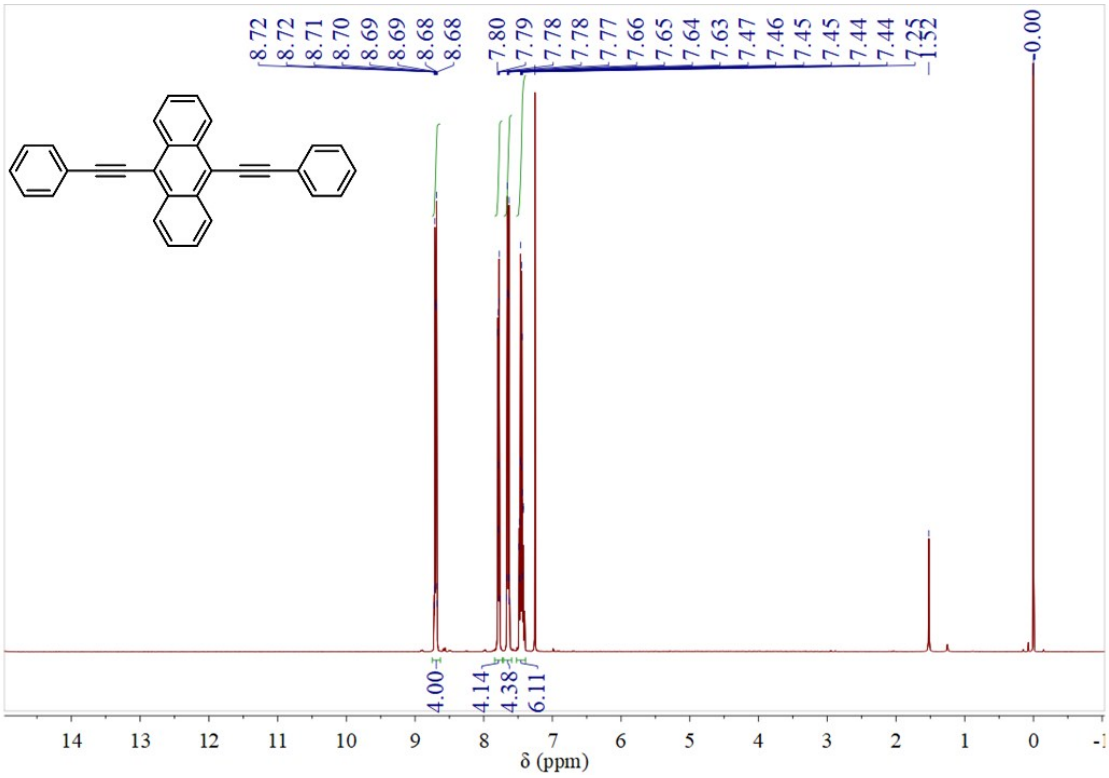


Fig. S1. The ^{1}H NMR spectrum of A1.

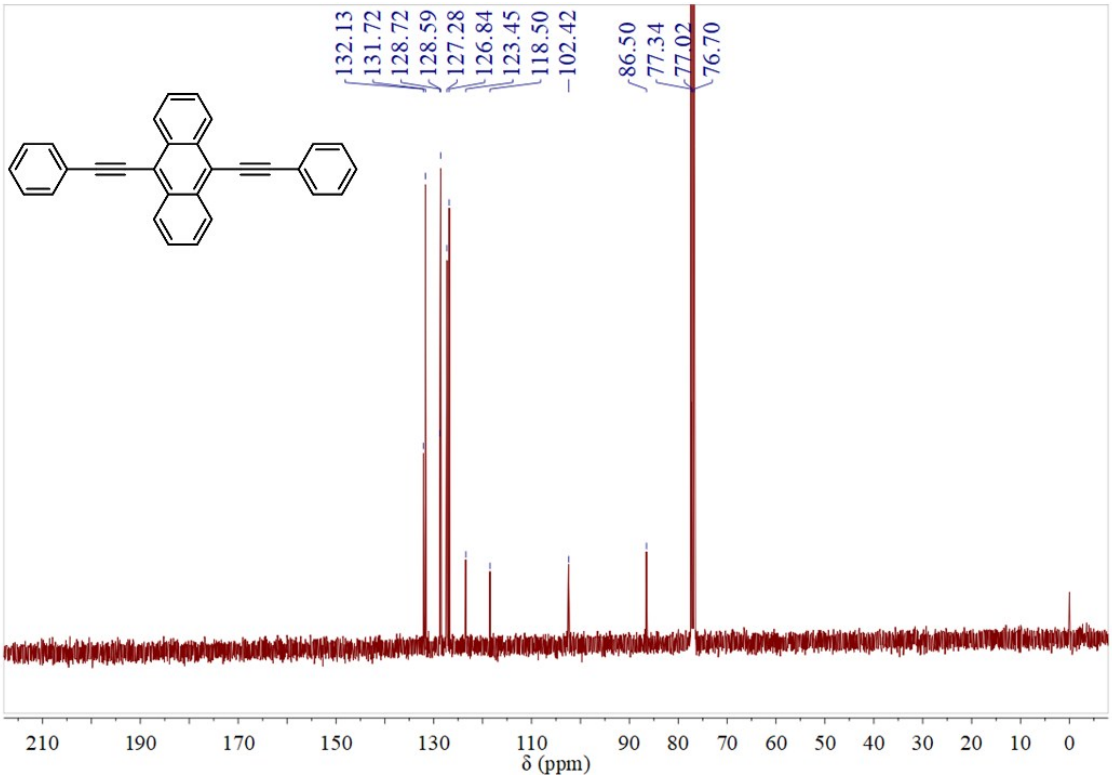


Fig. S2. The ^{13}C NMR spectrum of A1.

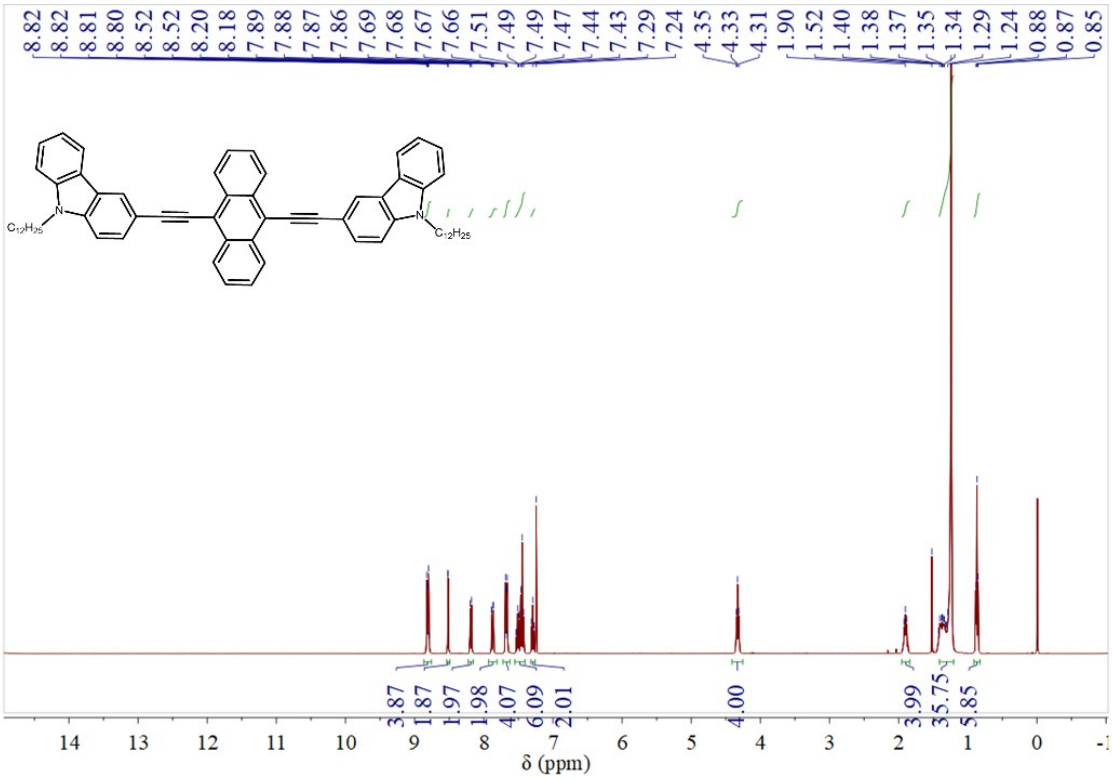


Fig. S3. The ^{1}H NMR spectrum of A2.

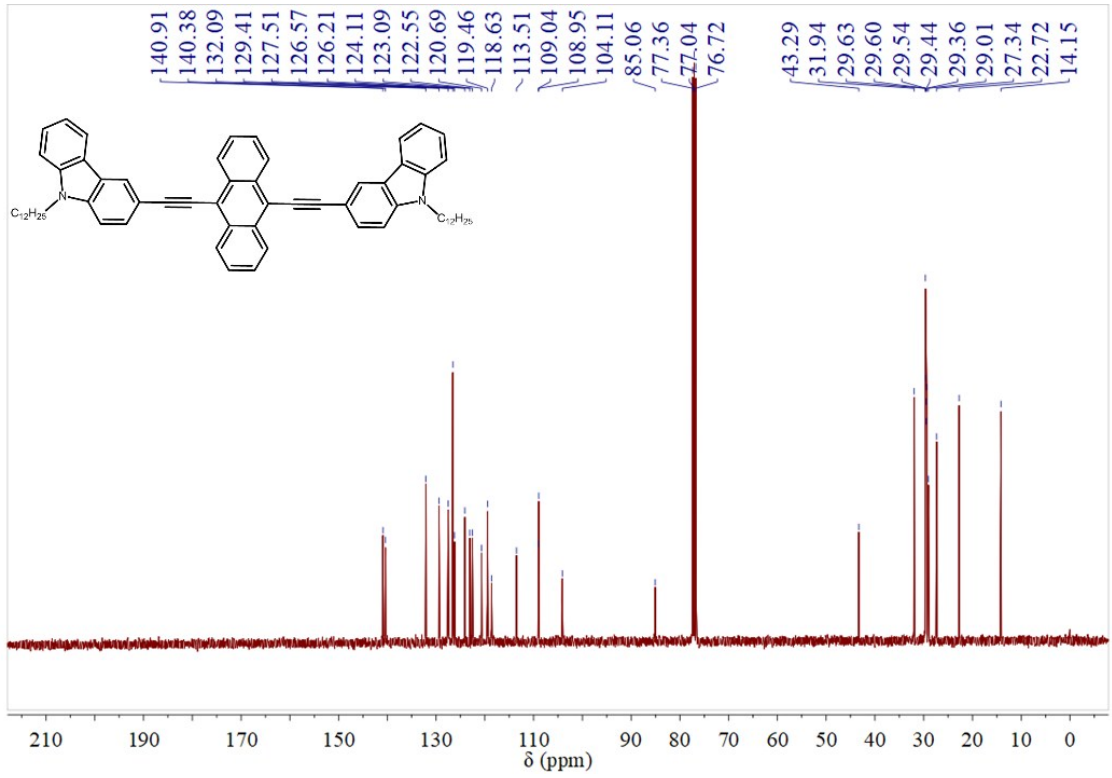


Fig. S4. The ^{13}C NMR spectrum of A2.

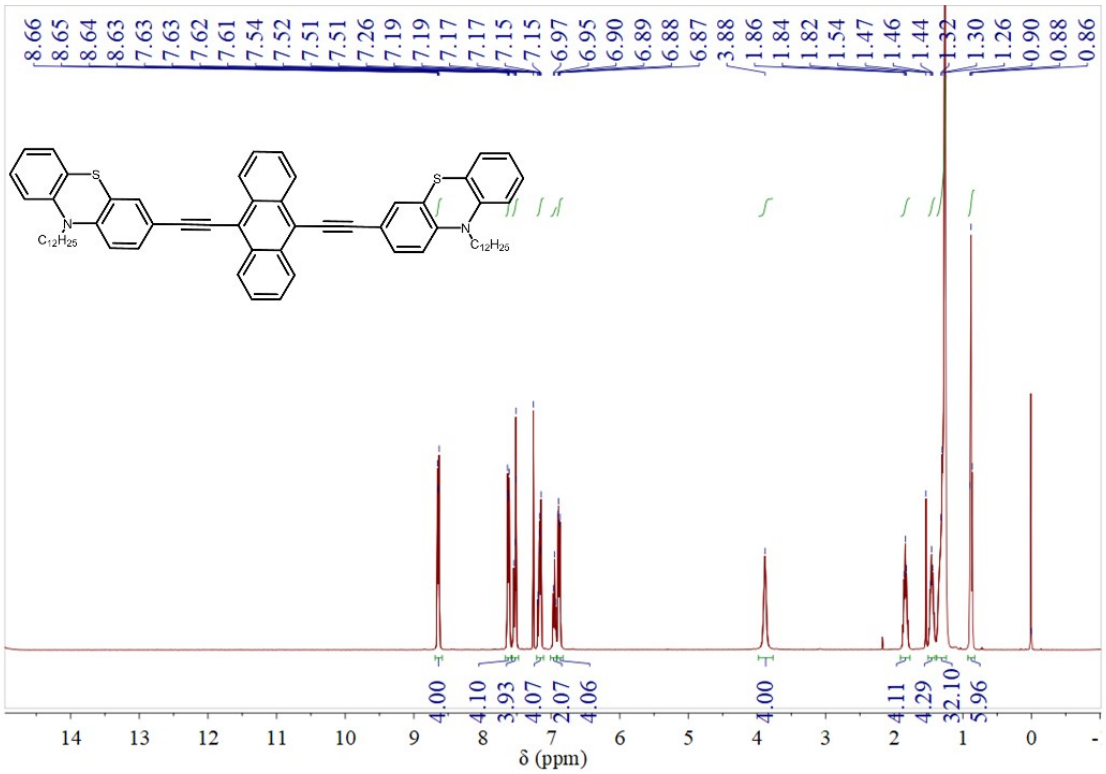


Fig. S5. The ^{1}H NMR spectrum of A3.

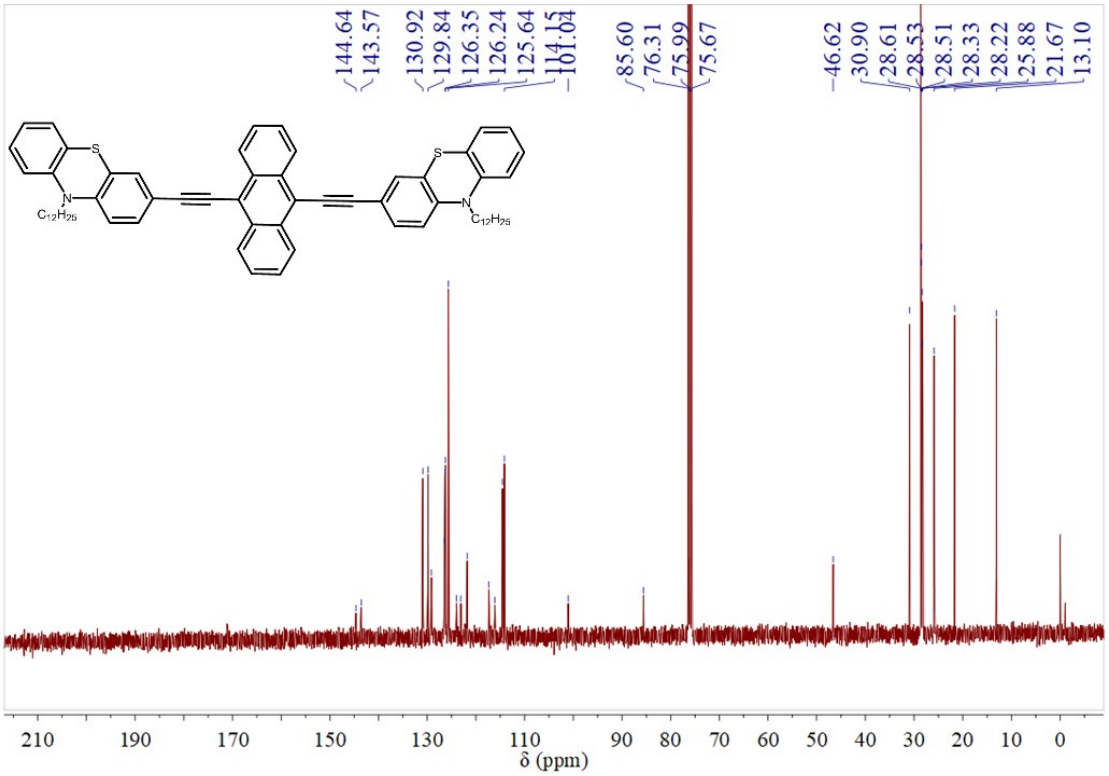


Fig. S6. The ^{13}C NMR spectrum of A3.

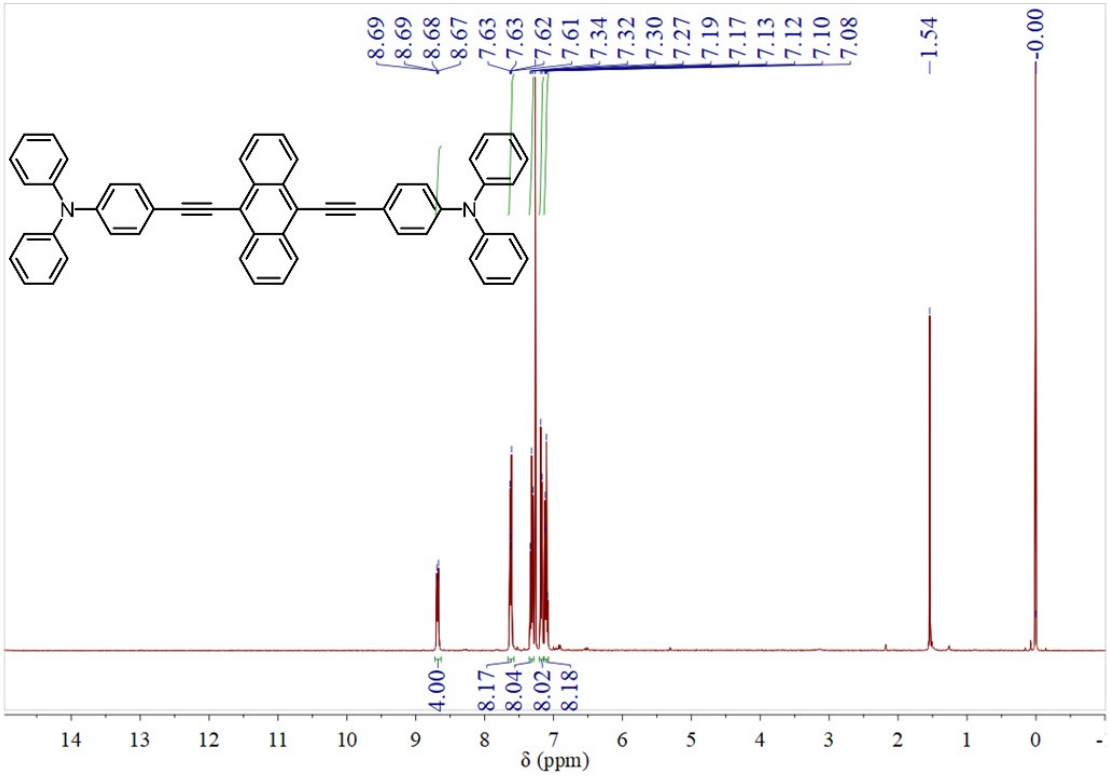


Fig. S7. The ^{1}H NMR spectrum of A4.

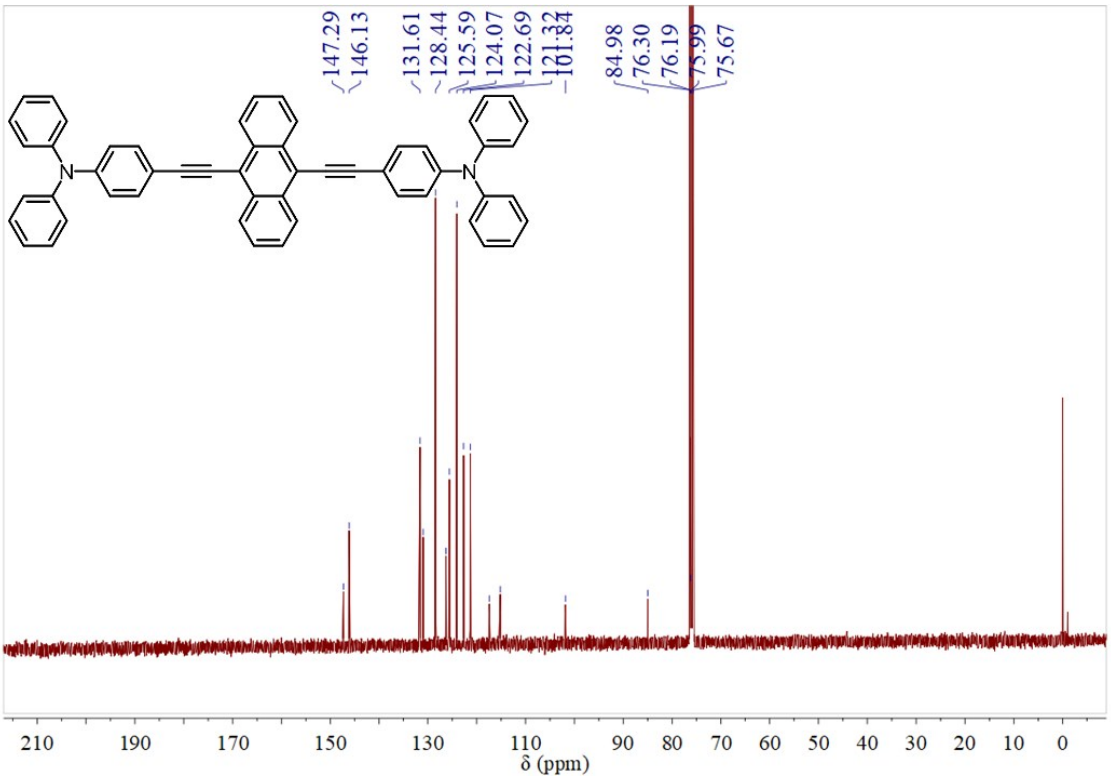


Fig. S8. The ^{13}C NMR spectrum of A4.

Table S1 Theoretical vertical transition energies, oscillator strength (f_{os}), involved molecular orbitals (MOs) and corresponding contribution

Molecular	Excited states	ΔE (eV)	λ(nm)	f_{os}	Involved MOs	Contribution
A1	1				HOMO→LUMO	99%
		2.7499	450.86	1.0349		
	3	4.2654	290.67	0.6369	HOMO-2→LUMO	74%
	10	4.7953	258.55	1.4308	HOMO-3→LUMO	41%
					HOMO→LUMO+3	57%
A2	1	2.6267	472.02	1.5213	HOMO→LUMO	96%
	4	3.9148	316.71	0.4299	HOMO-2→LUMO	61%
	7	4.3783	283.18	0.5820	HOMO→LUMO+3	81%
A3	1	2.6288	471.64	1.1028	HOMO→LUMO	92%
	3	3.6707	337.77	0.1896	HOMO-2→LUMO	72%
	7	4.3628	284.18	0.5662	HOMO-4→LUMO	35%
A4	1	2.5938	478	1.8626	HOMO→LUMO	91%
	3	3.6762	337.26	0.3961	HOMO-2→LUMO	83%
	5	4.2061	294.77	0.6384	HOMO→LUMO+2	66%

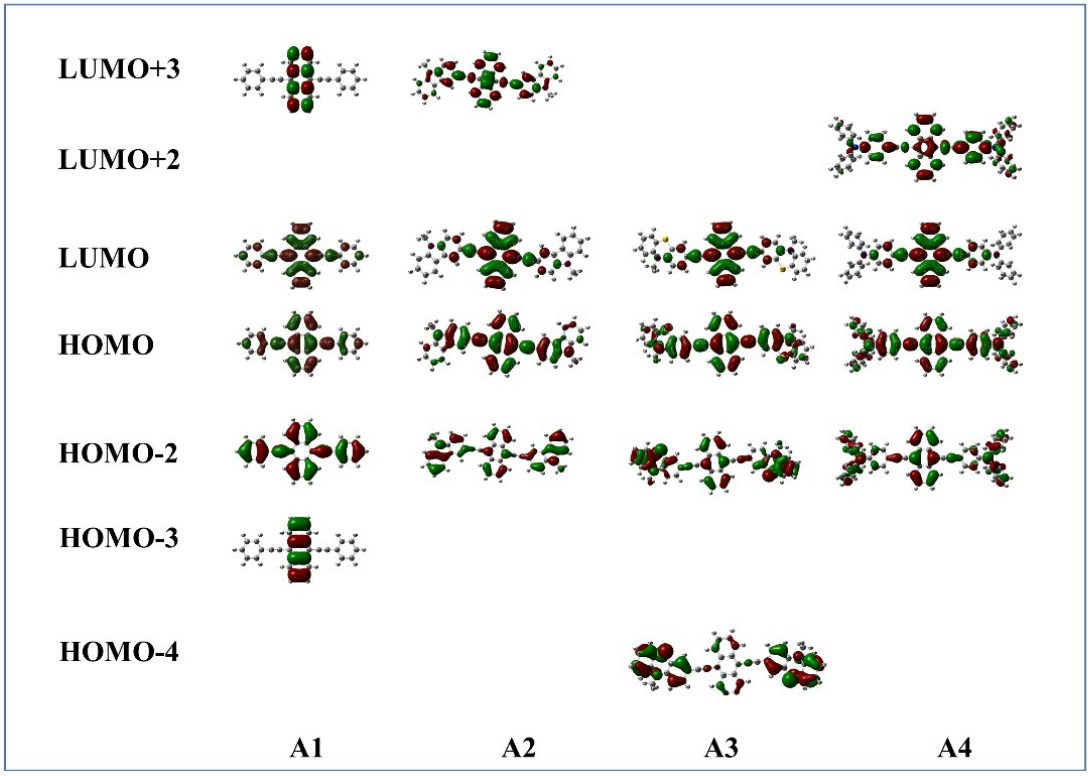


Fig. S9. Molecular orbitals of ANDs involved in different excited states.

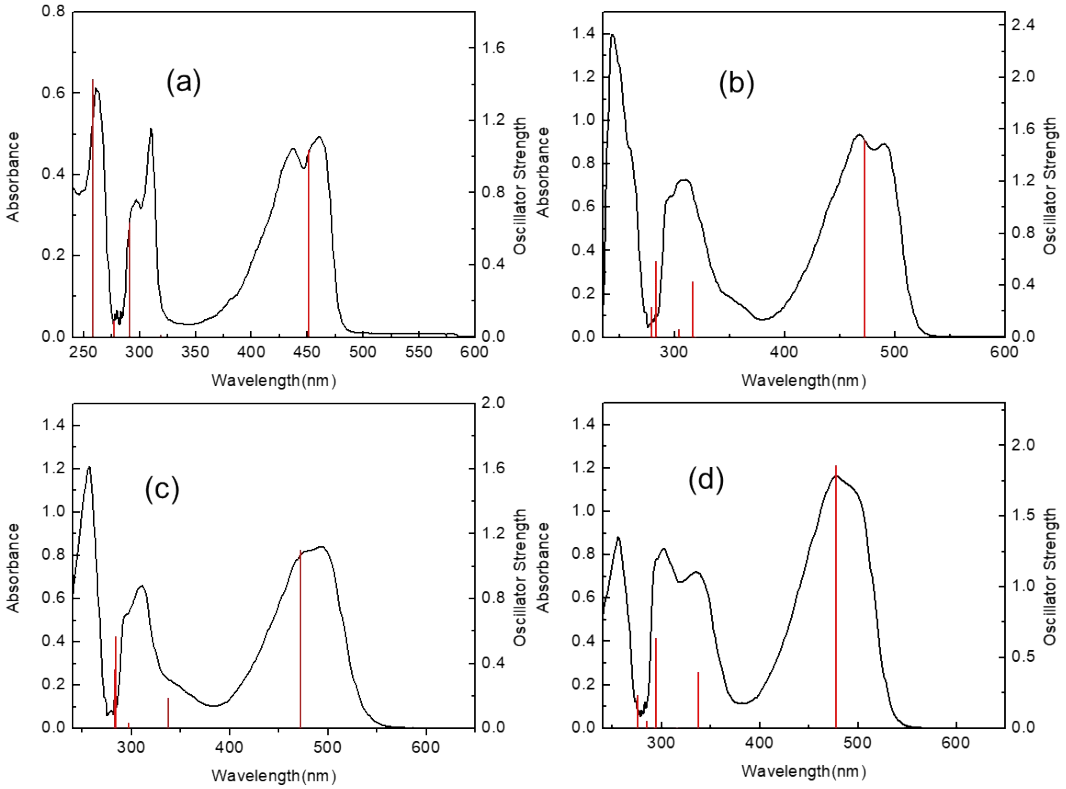


Fig. S10. Comparison of experimental UV-vis spectra and theoretical vertical transition energy. (a) A1, (b) A2, (c) A3, (d) A4. (The experimental spectra in black, calculated transition energies in red vertical lines).

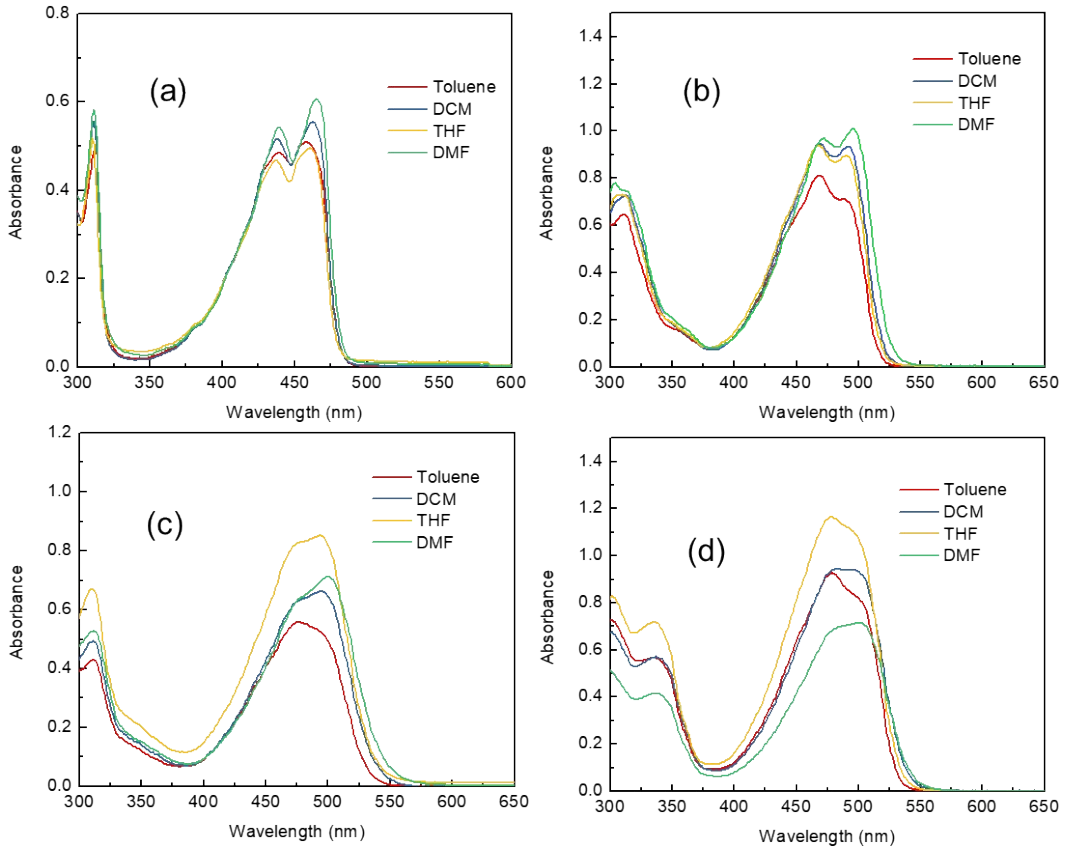


Fig. S11. Uv-vis absorption spectra of ANDs in different slovent (2.0×10^{-5} M). (a) A1, (b) A2, (c)

A3, (d) A4.

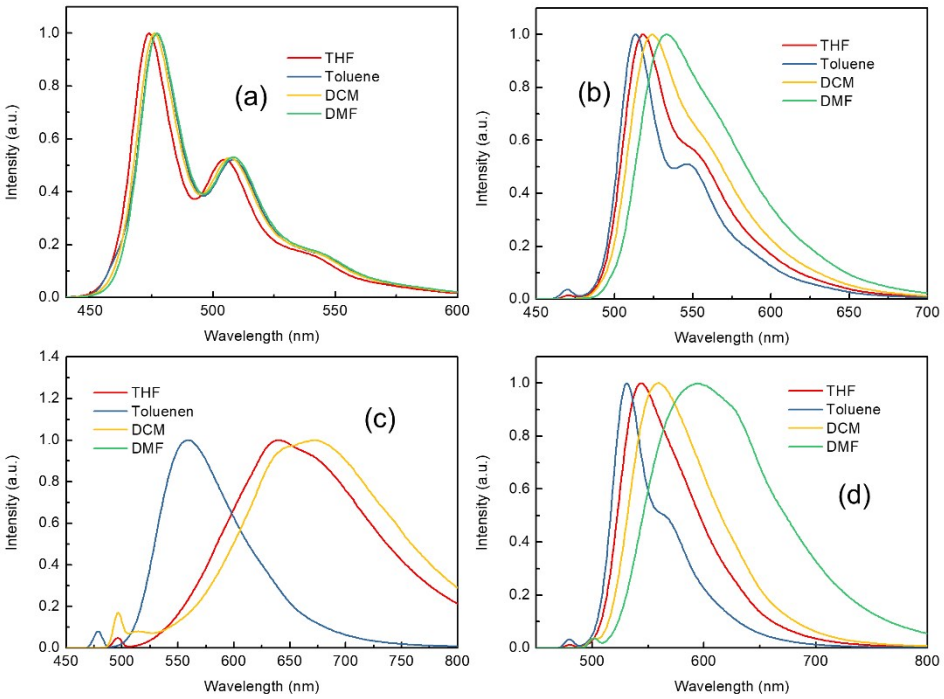


Fig. S12. Fluorescence emission spectra of ANDs in different slovent (2×10^{-5} M). (a) A1, (b) A2, (c) A3, (d)A4.

Table S2 One-photon optical properties of ANDs in different solvent

	Solvent	λ_{max1} (nm)	λ_{max2} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Stocks Shift (nm)
A1	Toluene	459	435	459	477	18
	DCM	462	438	462	476	14
	THF	461	437	461	474	13
	DMF	465	311	465	477	12
A2	Toluene	489	469	489	514	25
	DCM	491	469	491	524	33
	THF	490	468	490	518	28
	DMF	495	472	495	533	38
A3	Toluene	476	312	476	559	83
	DCM	496	311	496	671	175
	THF	494	311	494	638	144
	DMF	500	311	500	N [a]	N [a]
A4	Toluene	479	337	479	531	52
	DCM	485	337	485	559	74
	THF	478	336	478	544	66
	DMF	501	336	501	594	93

[a] No fluorescence signal was detected in DMF.

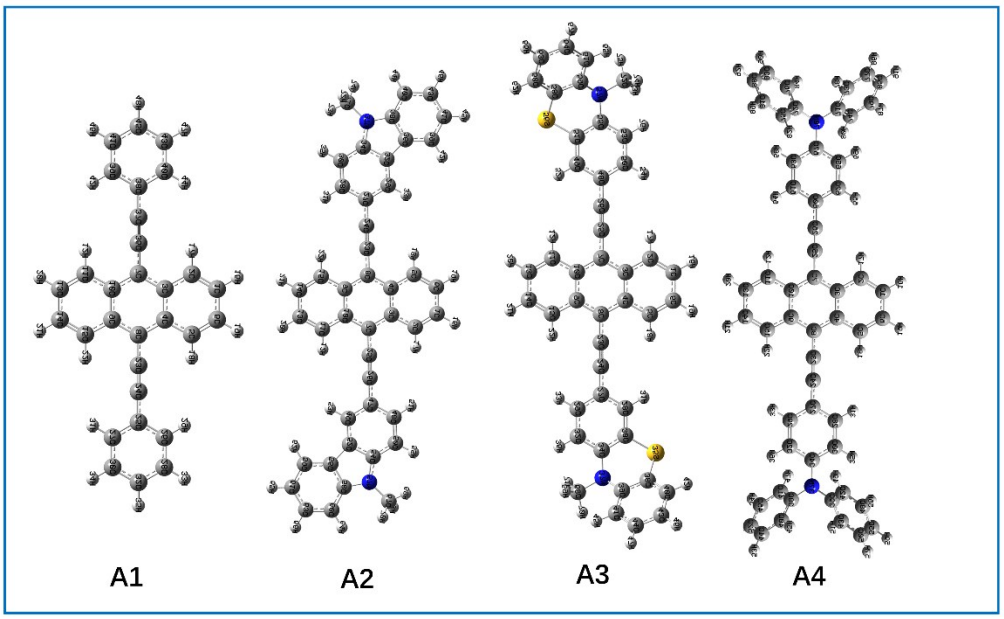


Fig. S13. Energy minimum structure of ANDs (ground states).

Table S3. The TPA cross-sections (TPACS) of ANDs at wavelengths ranging from 780 nm to 880 nm

Wavelength (nm)	σ_{TPA} (GM)*			
	A1	A2	A3	A4
880	37	66	330	293
860	25	53	323	481
840	25	117	506	617
820	90	512	616	1263
800	12	566	300	713
780	0	644	232	463

*The uncertainty of TPACS values may deviates from 15% because that a slope of 1.763 is too small to give the accurate uncertainty.

Table S4. The electrochemical data of Fc and sub-units in ANDs.

	E_{pa1} [a] (V)	E_{pc1} [a] (V)	$E_{1/2}$ [b] (V)	i_{pa1} [c] (uA)	i_{pc1} [c] (uA)
Fc	0.25	0.13	0.19	13.5	-11.5
AN	1.31	-	-	24.1	-
CZ	1.20	0.75	0.98	19.9	-4.0
PTZ	0.70	0.60	0.65	9.8	-7.34
TPE	0.99	0.86	0.93	16.9	-8.3

[a] E_{pa1} and E_{pc1} correspond to the peak potential at first anodic peak and corresponding cathodic peak, Redox potentials are reported in V (*vs*. SCE). [b] Half-wave potential, $E_{1/2} = (E_{pa1} + E_{pc1})/2$. [c] The peak current of first anodic peak and corresponding cathodic peak.

* The $E_{1/2}$ potential of Fc in DCM is reported as 0.38V (*vs*. SCE) in literature. As such, the potentials vs SCE in this work were calculated by E (*vs* Ag^+/Ag) + 0.19V.

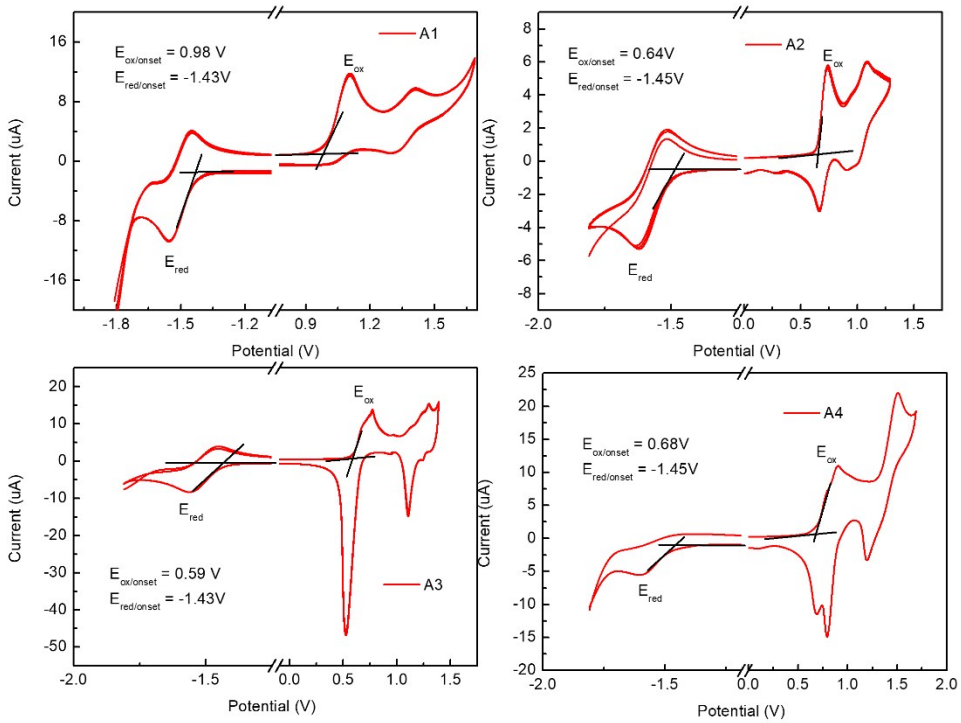


Fig. S14. The *E*onset ox and *E*onset red obtained according to the literature method (*vs*. SCE).

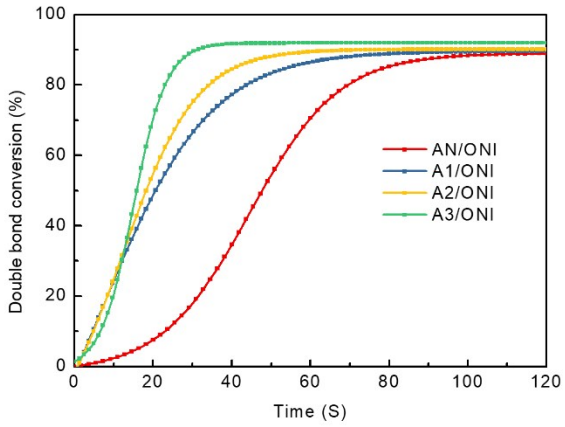


Fig. S15. Photopolymerization profiles of HDDA in the presence of ANDs/ONI (ONI: 2.0 wt%; ANDs: 0.2 wt%) and AN/ONI (ONI: 2.0 wt%; AN: 0.2 wt%) under violet LED.

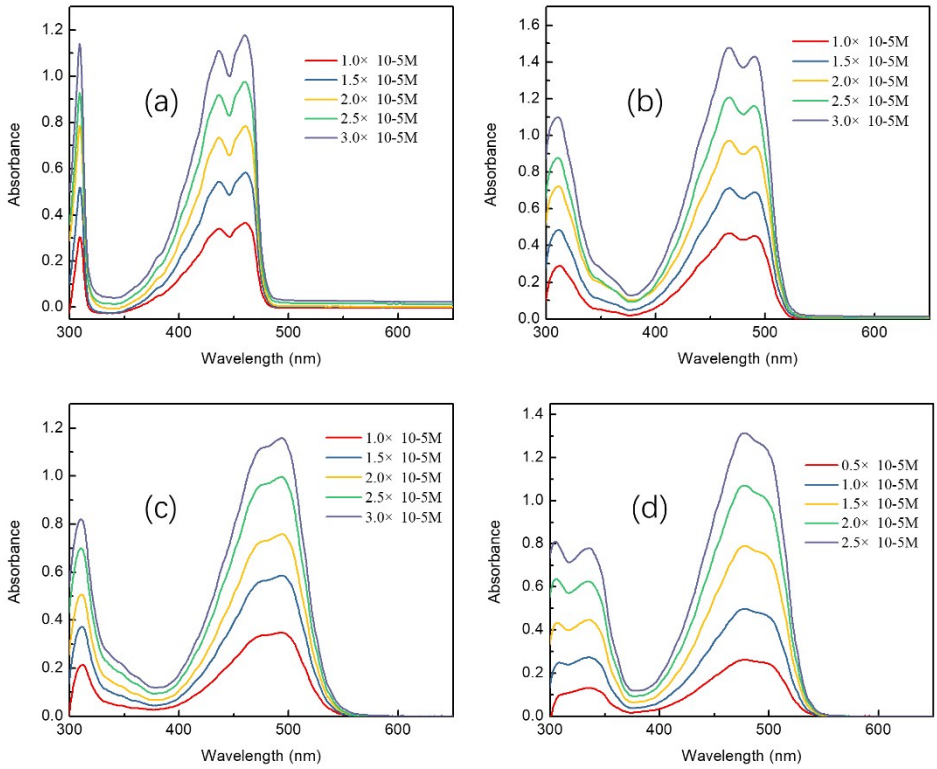
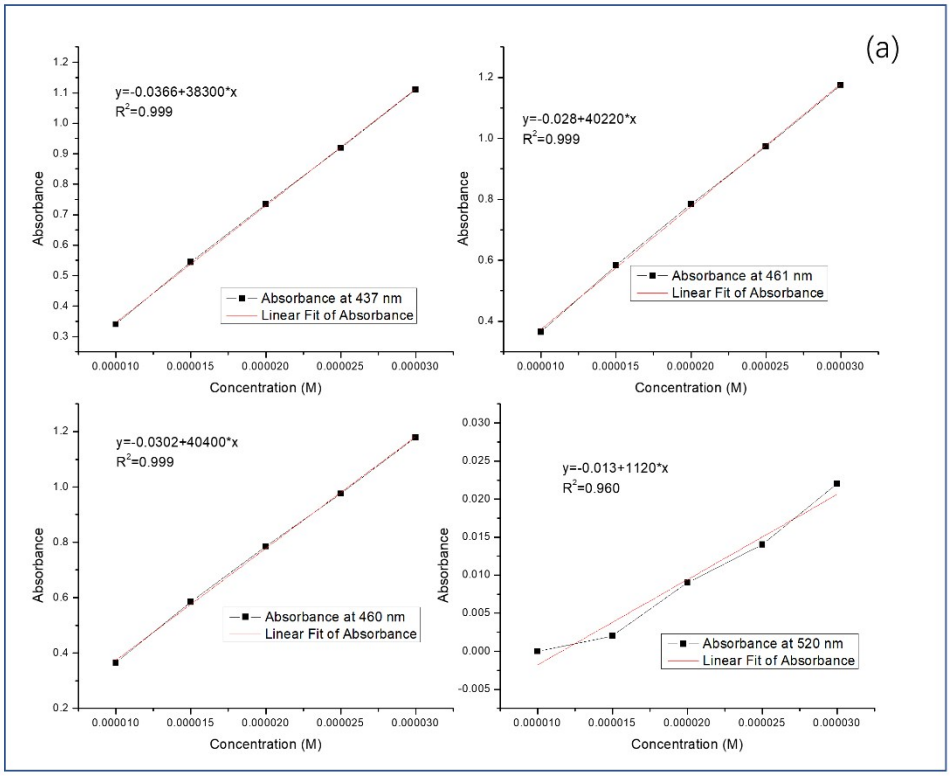
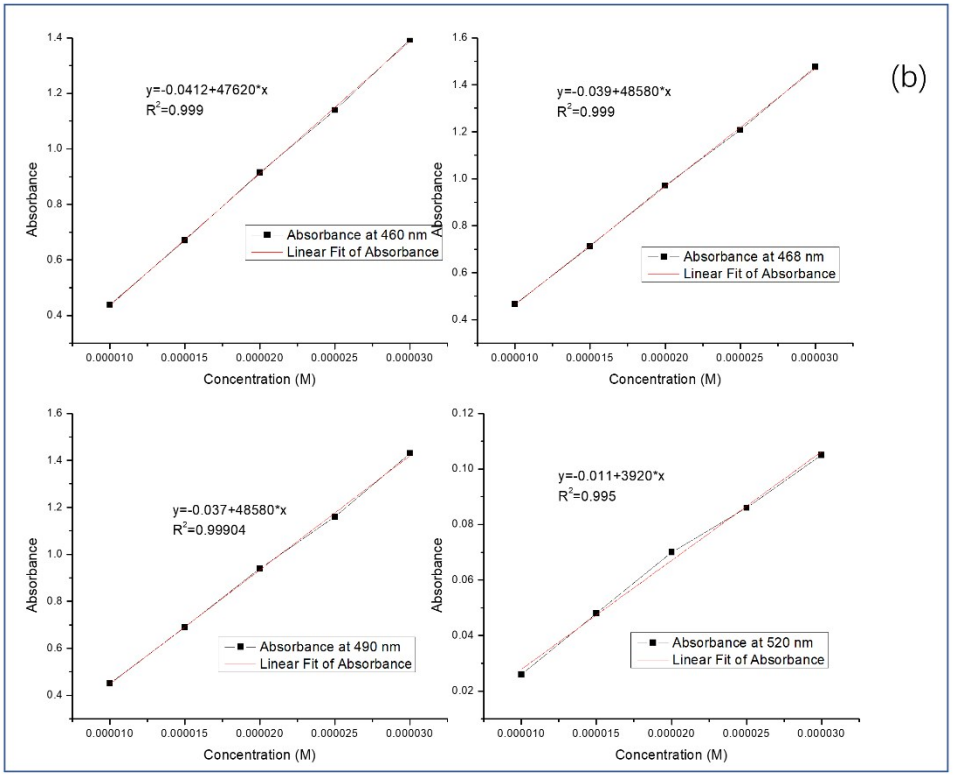
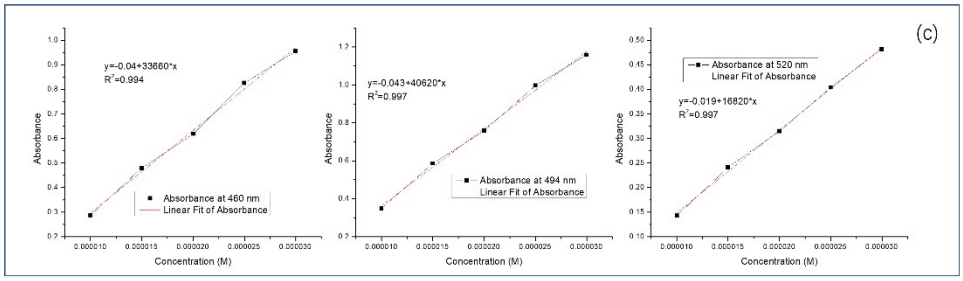


Fig. S16. Uv-vis spectra of THF solution with different ANDs concentration. (a) A1; (b) A2; (c) A3; (d) A4.







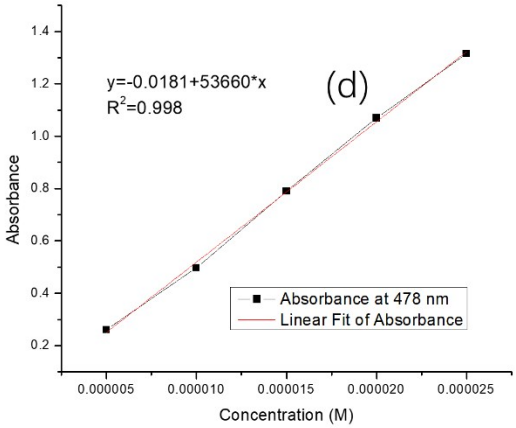


Fig. S17. Molar extinction coefficient at specific wavelength calculated by using the Lambert-Beer law. (a) A1; (b) A2; (c) A3; (d) A4.