Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Multi-stimuli responsive behaviors of two TPE-based tautomers in solid state and in solution

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Experimental information

1. Materials and instrumentations

All solvents and reagents (analytical grade and spectroscopic grade) were used as received. All the metal salts used in the experiments were LiCl, NaCl, KNO_3, $CaCl_2$, $MgCl_2{\cdot}6H_2O$, $Al(ClO_4)_3{\cdot}9H_2O$, $CrCl_3{\cdot}6H_2O$, $Mn(ClO_4)_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $Ni(ClO_4)_2{\cdot}6H_2O$, $FeCl_3$, $Cu(ClO_4)_2{\cdot}6H_2O$, $Zn(ClO_4)_2{\cdot}6H_2O$, $Cd(ClO_4)_2{\cdot}6H_2O$, $Hg(ClO_4)_2{\cdot}3H_2O$ and $Pb(ClO_4)_2{\cdot}3H_2O$. C, H and N elemental analyses were collected with a Vario EL elemental analyser. Fourier transform infrared (FT-IR) spectra were measured on an Avatar 360 FT-IR spectrometer using KBr pellets in 4000-400 cm^{-1}. The melting point was determined by WRX-4 micro melting point meter. The UV–Vis absorption spectra were measured by UV-2450 spectrophotometer. The fluorescence spectra were recorded on a FS5 fluorescence spectrophotometer with a quartz cuvette (path length = 1 cm), and lifetime was measured on a FLS980. ^1H NMR spectra were recorded on a Bruker Avance III 600 MHz spectrometer. DLS (dynamic light scattering) data and SEM images were obtained on Brookhaven Zeta Plus Zeta Potential Analyzer and SEM S-4800 Hitachi, respectively. Differential scanning calorimetry (DSC) was carried out using a Mettler DSC 1 instrument. Powder X-Ray diffraction (PXRD) patterns were performed on an X'Pert PRO MPD diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 25°C. Single crystals data was collected on a Bruker Smart APEXII CCD diffractometer with Cu-Kα radiation (λ = 1.54184 Å) at 100 K. The crystal structures were solved by the direct method and refined using the Olex2 program. Hydrogen atoms were placed in calculated positions.

2. Synthesis of a TPE-based Schiff-base (HL)

4-(1,2,2-Triphenylethenyl)benzenamine (0.05 mmol, 0.0174 g), 2-hydroxy-1-naphthaldehyde (0.05 mmol, 0.0086 g) and 3 ml methanol were sealed in 25 ml Teflon-lined autoclave and heated at 80°C for 1 day, and then cooled to room temperature. Orange flake crystals (HL^k) were obtained (yield 80.5%). Anal. Calcd: C, 88.59%, H, 5.43%, N, 2.79%; Found: C, 88.34%, H, 5.34%, N, 2.79%. IR (KBr pellet, cm^{-1}): 3448s, 3051w, 2372m, 1624s, 1585s, 1385s, 1327s, 1157w, 1080w, 968w, 826w, 748m, 698s. ^1H NMR (600 MHz, THF-d_8): δ=15.43 (s, 0.82H), 10.83 (s, 0.18H), 9.64 – 9.55 (m, 1H), 8.31 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 9.1 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.33 – 7.22 (m, 3H), 7.15 – 7.01 (m, 18H) ppm. Melting point: 252.5-253.0 °C. When 6 ml instead of 3 ml methanol was used and heated at 80°C for 3 day, the yellow flake crystals (HL^e) were obtained (yield 80.6%). Anal. Calcd : C, 88.59%, H, 5.43%, N, 2.79%; Found: C, 88.40%, H, 5.15%, N, 2.71%. IR (KBr pellet, cm^{-1}): 3402s, 3021w, 2368s, 2342m, 1620w, 1566s, 1381m, 1323m, 1177m, 818m, 745m, 698s. ^1H

NMR (600 MHz, THF-d_8): δ=15.43 (s, 0.84H), 10.82 (s, 0.16H), 9.61 – 9.55 (m, 1H), 8.31 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 9.1 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 5.9 Hz, 2H), 7.14 – 7.01 (m, 18H) ppm. Melting point: 263.8-264.2 ℃. ESI-MS m/z, ion: 502.1478 $[HL+H]^+$.

3. X-ray analysis

The single-crystal X-ray diffraction data of tautomer (HL^e and HL^k) crystals of HL before and after grinding and HL^e crystals obtained from fumed HL^k crystals were collected on the Bruker APEX II CCD diffractometer with Cu-Kα radiation (λ = 1.54184 Å) at 100 K. The crystal structures were solved and refined using the Olex2 program and all hydrogen atoms were added automatically. Crystal data and structure refinement parameters for the two tautomers of HL are summarized in Table S1. The pictures were created with the Mercury/Diamond program.

Figures

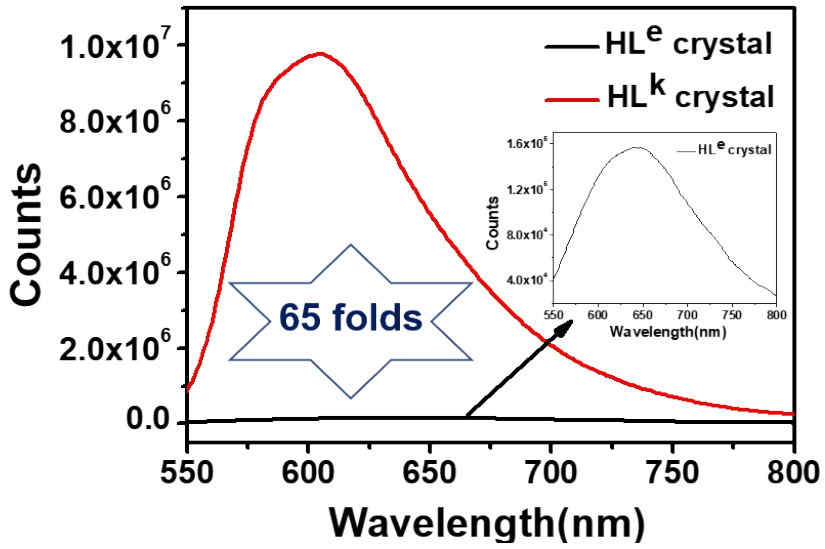


Figure S1. Fluorescence spectra of HL^e and HL^k in the crystal state.

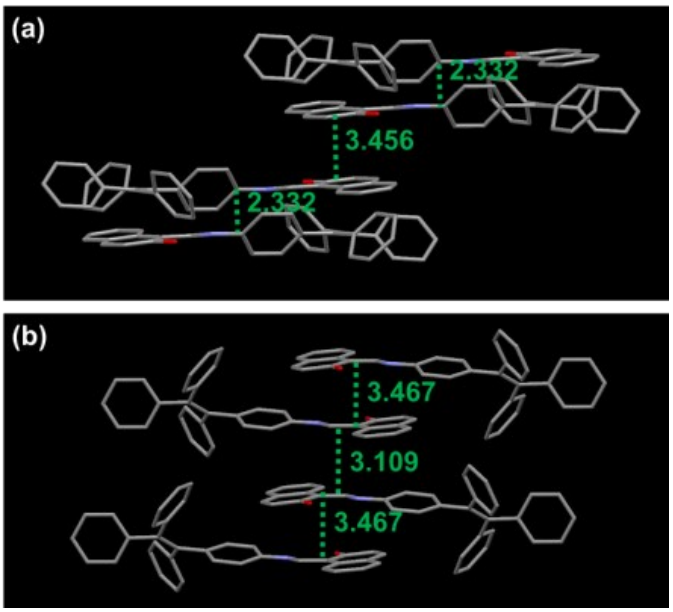


Figure S2. Molecular packing modes of (a) HL^e, (b) HL^k.

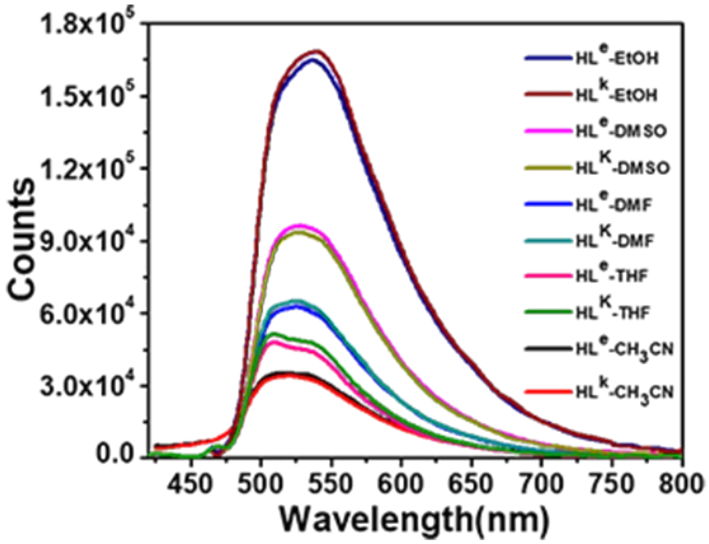


Figure S3. The fluorescence spectra of HL^e and HL^k (10^{-5} M) in different organic solvents, excited at 455 nm in EtOH, DMSO and DMF, excited at 410 nm and 415 nm in THF and CH_3CN, respectively.

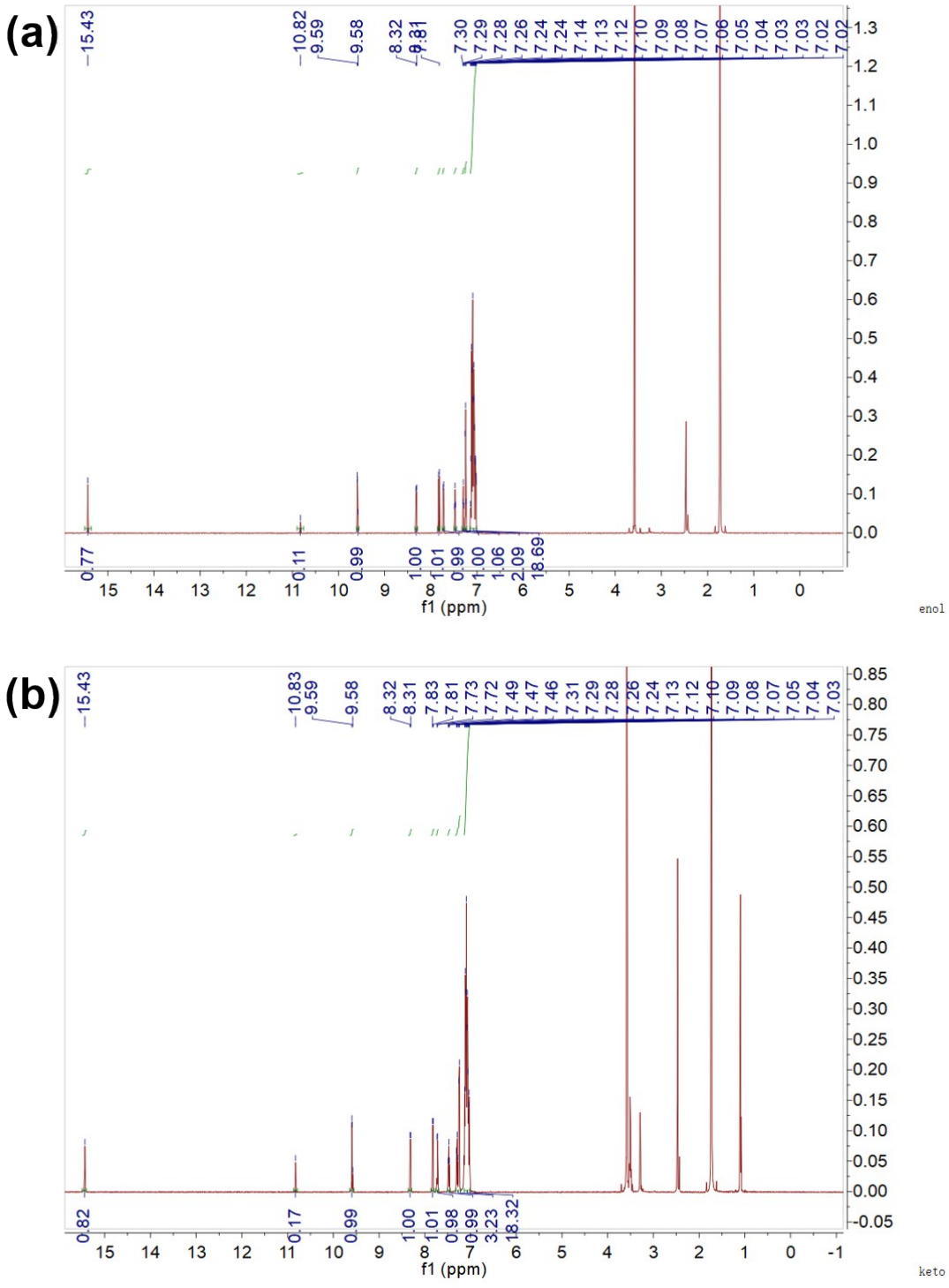


Figure S4. ^{1}HNMR of (a) HL^{e} and (b) HL^{k} in THF-d8.

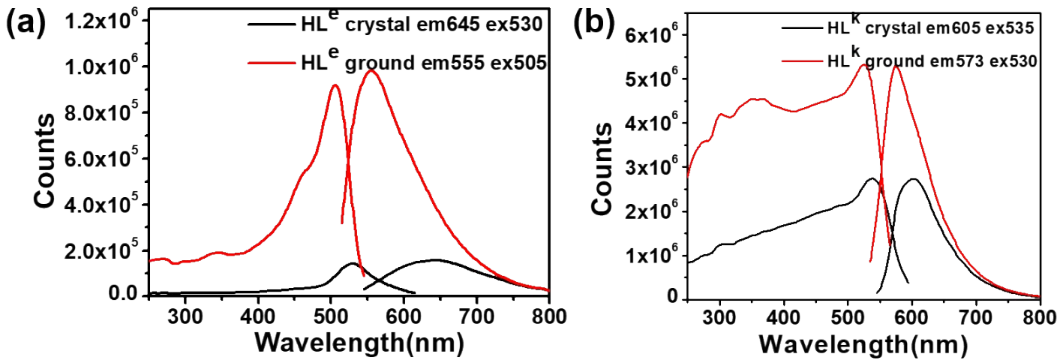


Figure S5. Fluorescence excitation and emission spectra of (a) HL^e and (b) HL^k.

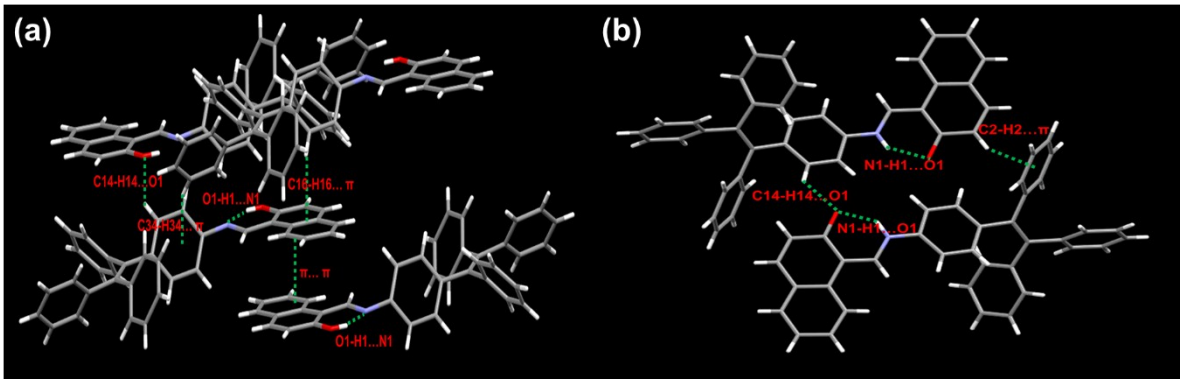


Figure S6. Molecular packing diagram of (a) HL^e and (b) HL^k.

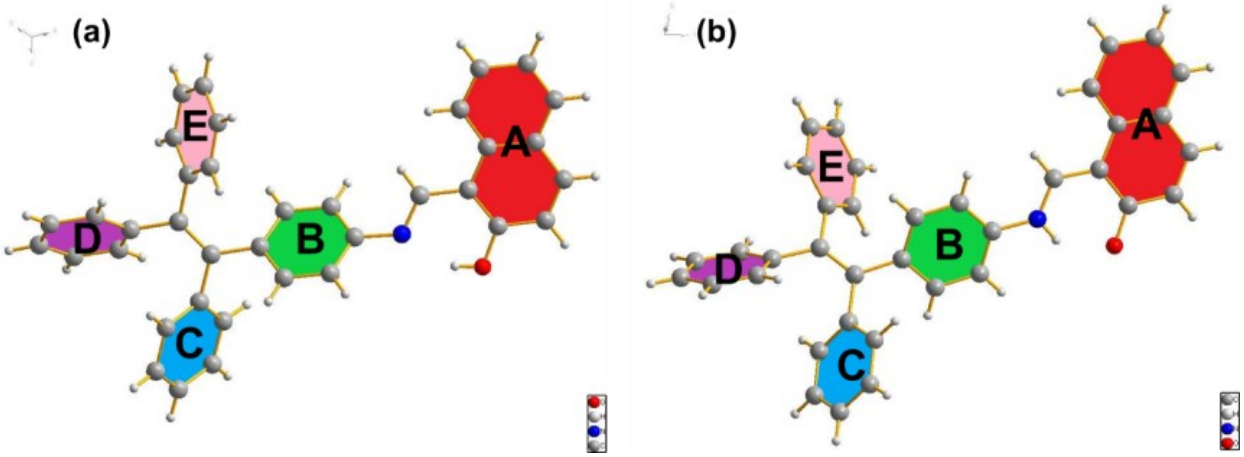


Figure S7. Molecular structure diagrams of (a) HL^e and (b) HL^k.

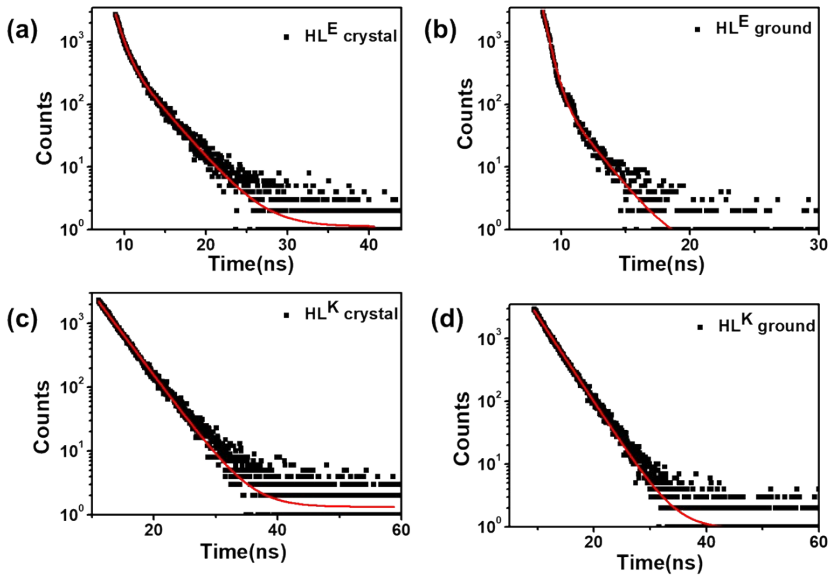


Figure S8. PL decay curves for the solid states of HL^e and HL^k.

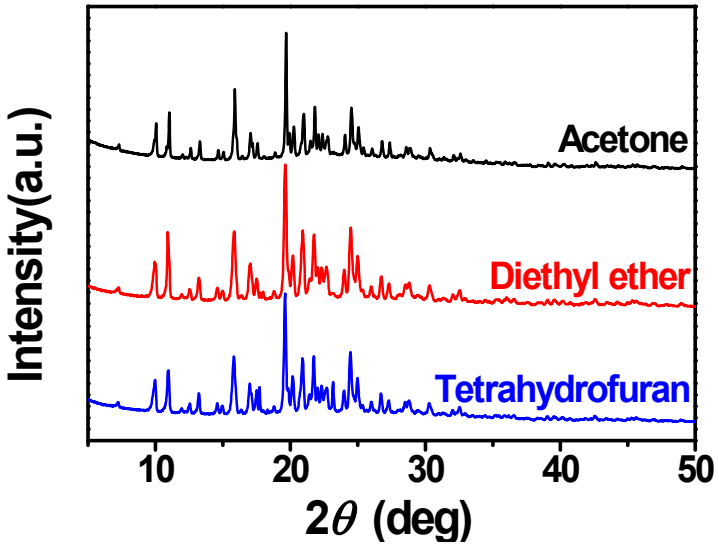


Figure S9. XRD patterns of HL^k to crystals of HL^e transformation via acetone, diethyl ether and tetrahydrofuran vapors.

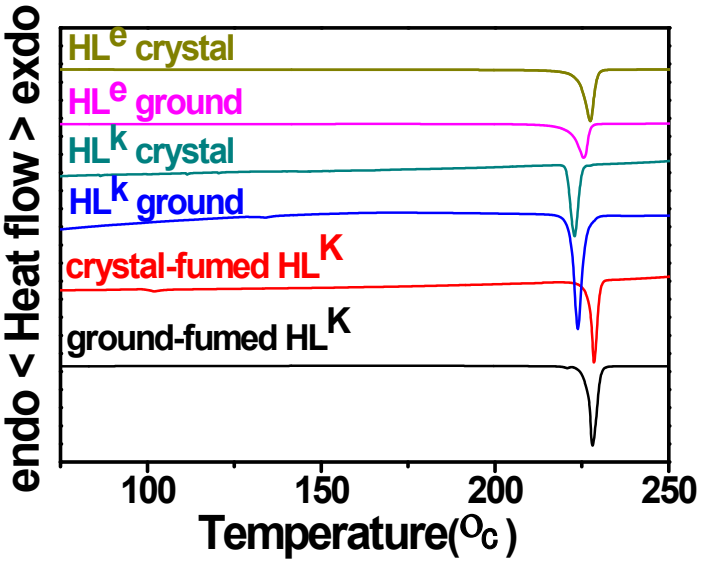


Figure S10. DSC curves of HL^e and HL^k samples.

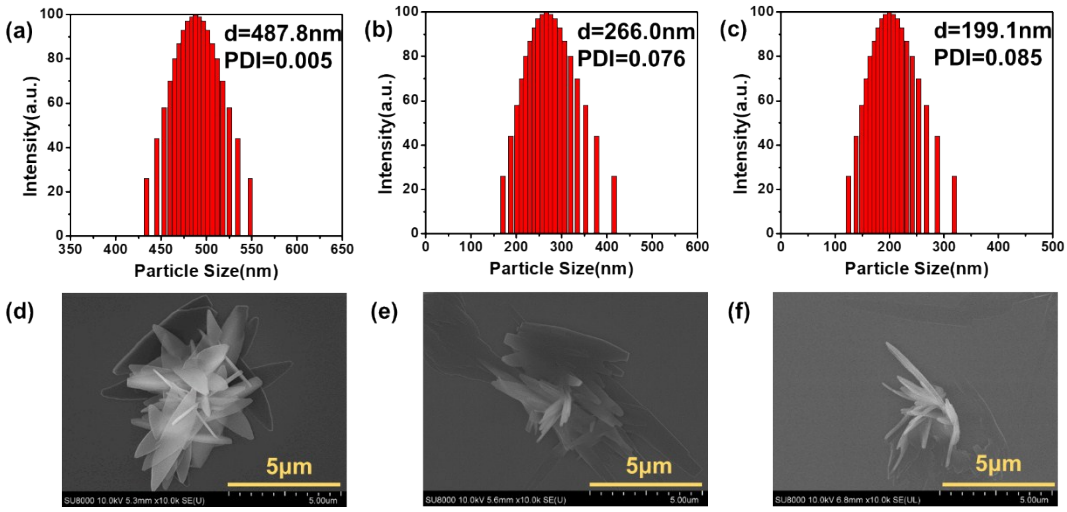


Figure S11. DLS data of HL^e (50 μM) in THF/H_2O: (a) 70% H_2O, (b) 80% H_2O and (c) 90% H_2O. SEM images of HL^e (50 μM) in THF/H_2O: (a) 70% H_2O, (b) 80% H_2O and (c) 90% H_2O.

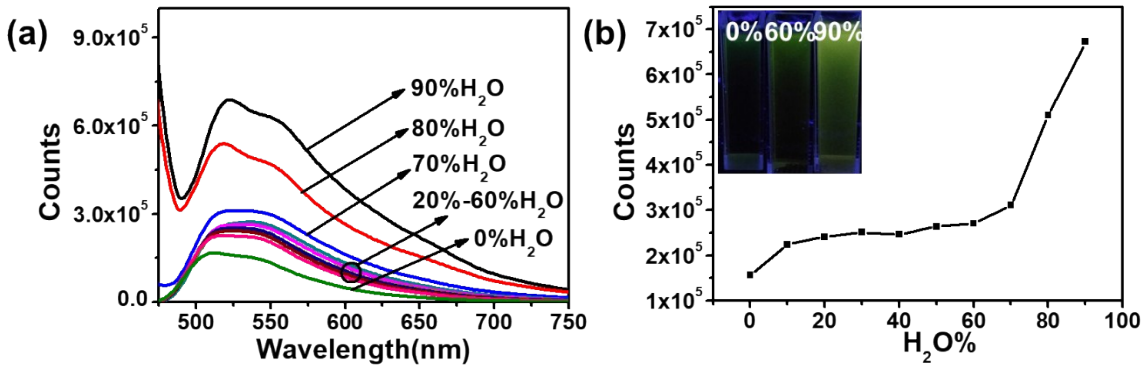


Figure S12. (a) Fluorescent spectra of HL^k (50 μM) in THF/H_2O with different ratio (v:v), excited by 450 nm. (b) Fluorescence intensity of HL^k (50 μM) at 535 nm in THF/H_2O with different ratio (v;v).

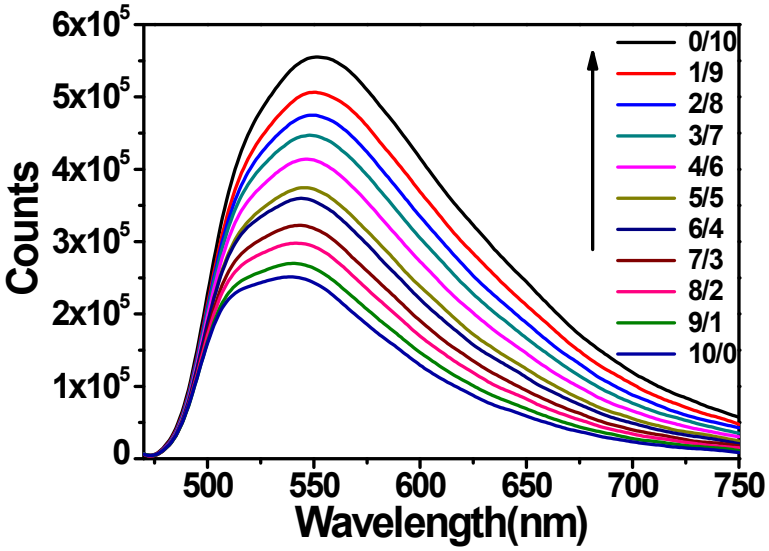


Figure S13. Fluorescent spectra of HL^e (10 μM) in $C_2H_5OH/(CH_2OH)_2$ with different ratio (v:v) excited by 460 nm.

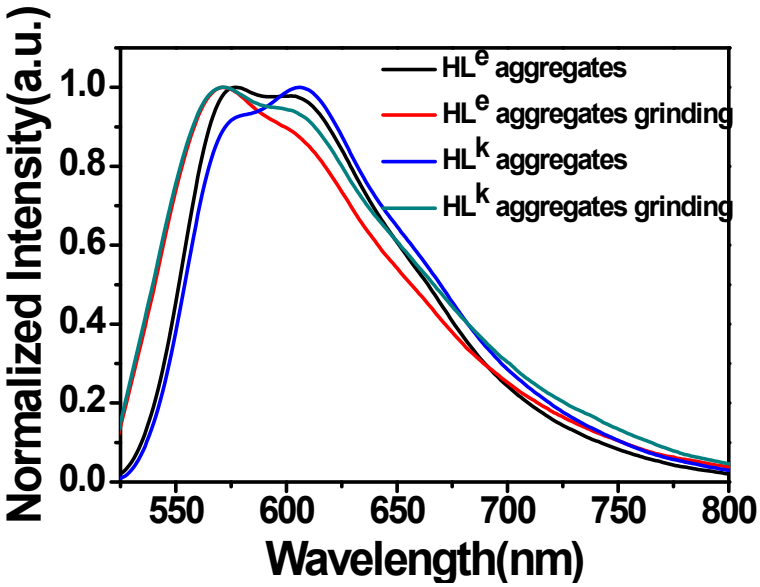


Figure S14. Soild fluorescent spectra of Agg-HL^e and Agg-HL^k obtained in THF/H_2O (3:7) and of further grinding samples, excited at 510nm.

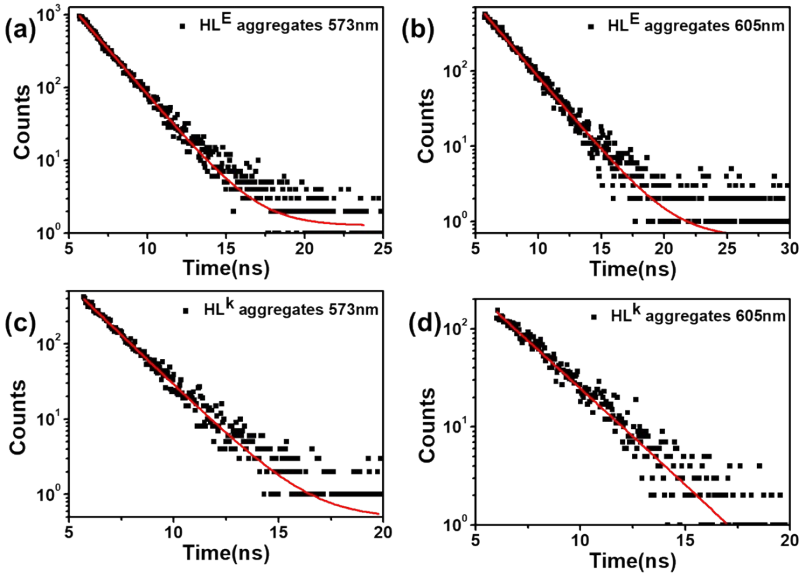


Figure S15. Fluorescence decay of Agg-HL^e (a, b) and Agg-HL^k (c, d), monitored at 573 nm (a, c) and at 605 nm (b, d).

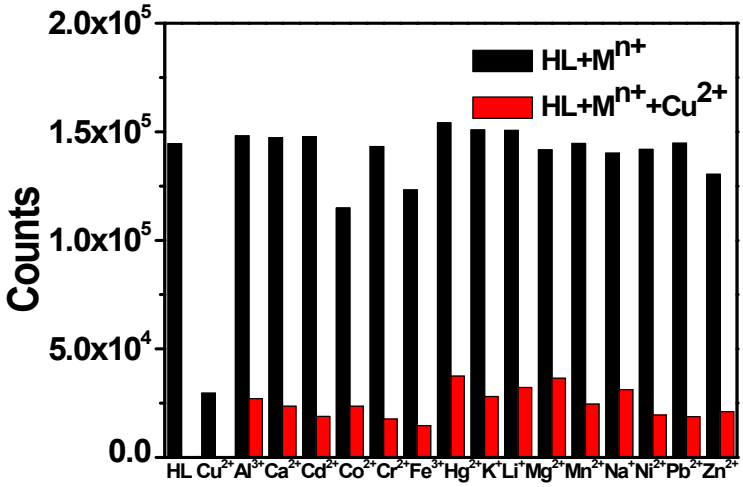


Figure S16. Fluorescence intensity of complexes of HL and Cu^{2+} in the presence of various metal ions at 535 nm in ethanol. Black bars: HL (10 μM) with 1.0 equiv. metal ions stated. Red bars: HL (10 μM) with 1.0 equiv. Cu^{2+} and 1.0 equiv. other metal ions stated.

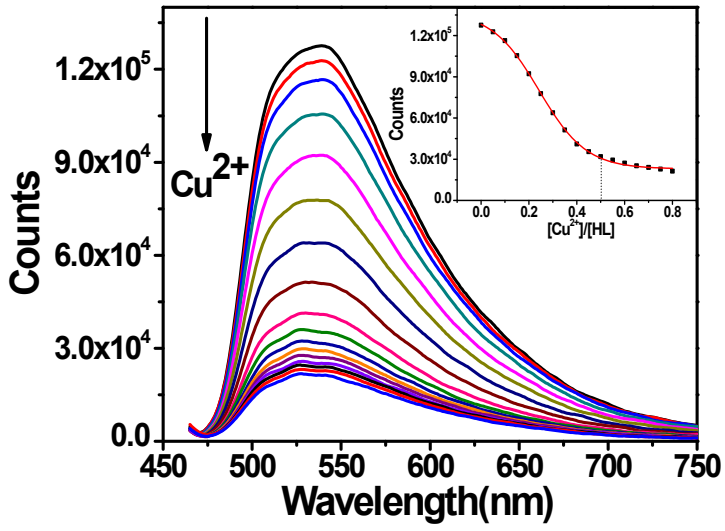


Figure S17. Changes of fluorescence spectra of 10 μM HL upon addition of Cu^{2+} ions (0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80 equiv. Cu^{2+}) in ethanol. Inset: Fluorescence intensity at 535 nm as a function of $[Cu^{2+}]/[HL]$.

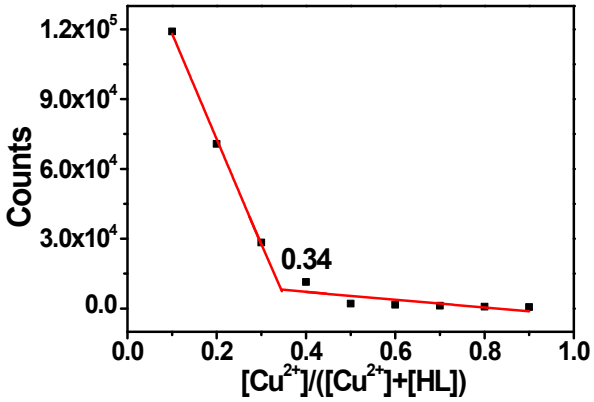


Figure S18. Job's plot for the determination of the stoichiometry of Cu^{2+}: HL in ethanol.

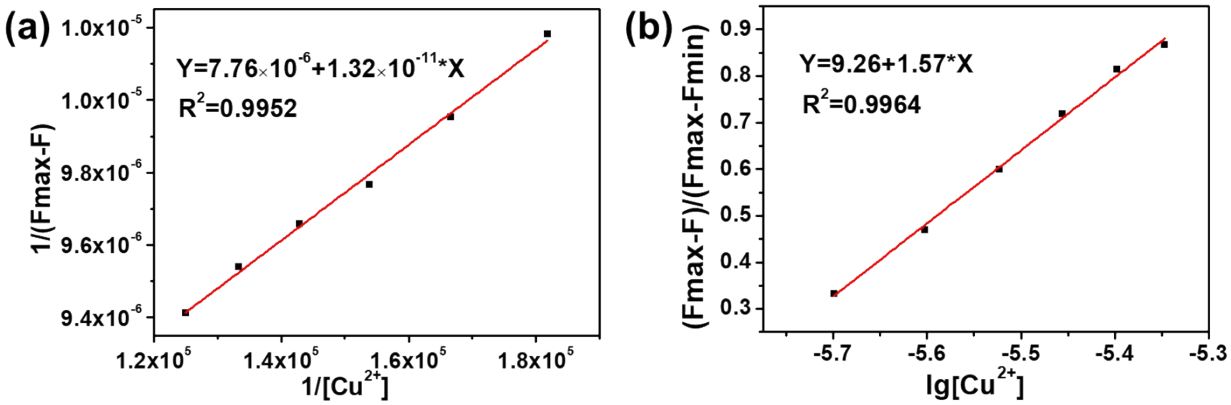


Figure S19. (a) Estimation of association constant by Benesi-Hildebrand (B-H) plot for 2:1 stoichiometry of complexation between HL and Cu^{2+} in ethanol. (b) Normalized response of fluorescence signal at 535 nm to changing Cu^{2+} concentrations.

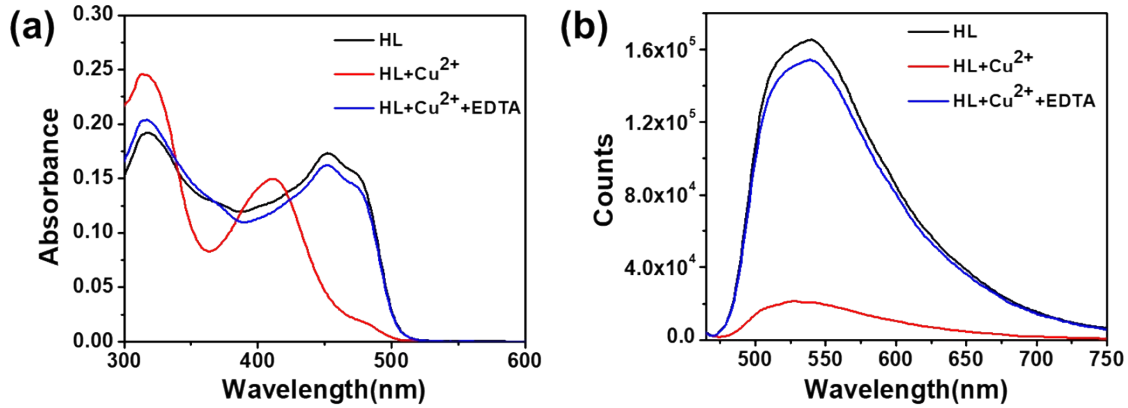


Figure S20. (a) The absorption spectra of HL (10 μM) before and after the equal addition of Cu^{2+} and EDTA in EtOH. (b) The fluorescence spectra of HL (10 μM) before and after the equal addition of Cu^{2+} and EDTA in EtOH, excited by 455nm.

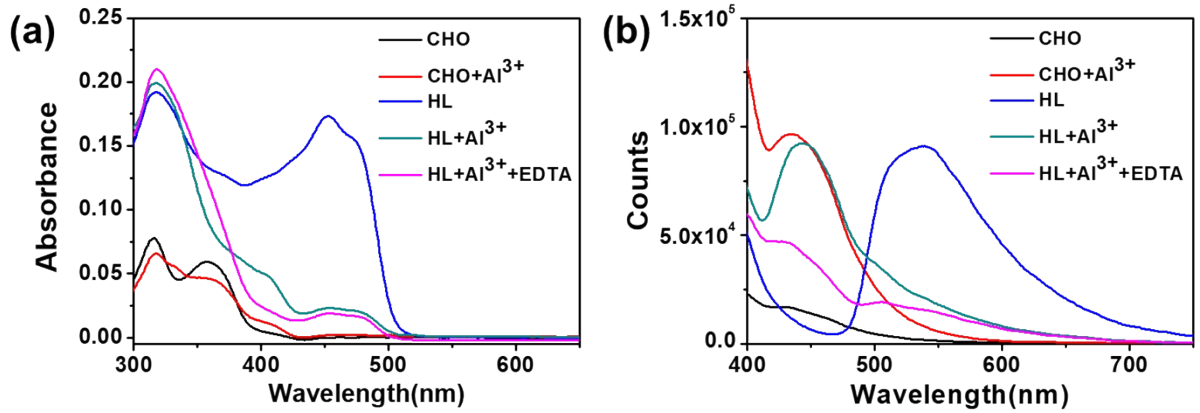


Figure S21. (a) The absorption spectra of HL and CHO (10 μM) before and after the equal addition of Al^{3+} and EDTA in ethanol. (b) The fluorescence spectra of HL and CHO (10 μM) before and after the equal addition of Al^{3+} and EDTA in ethanol, excited by 335nm.

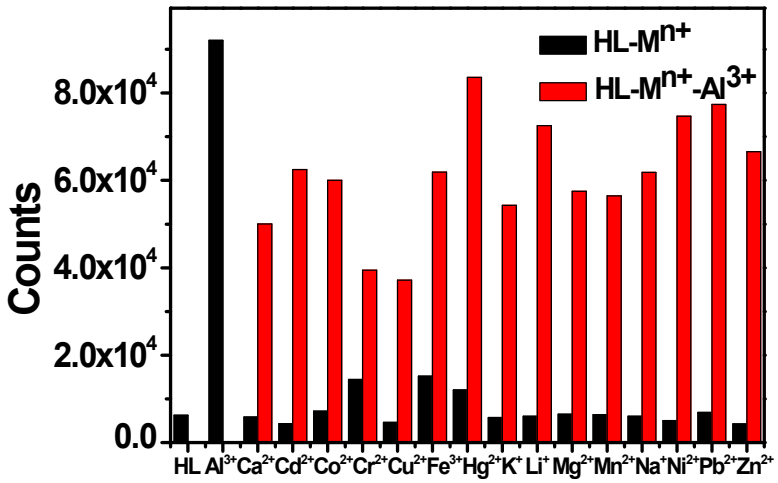


Figure S22. Fluorescence emission intensity of complexes of HL and Al^{3+} in the presence of various metal ions at 445 nm. Black bars: HL (10 μM) with 1.0 equiv. of the metal ions stated. Red bars: Solutions of HL (10 μM) with 1.0 equiv. of Al^{3+} and 1.0 equiv. of the other metal ions stated.

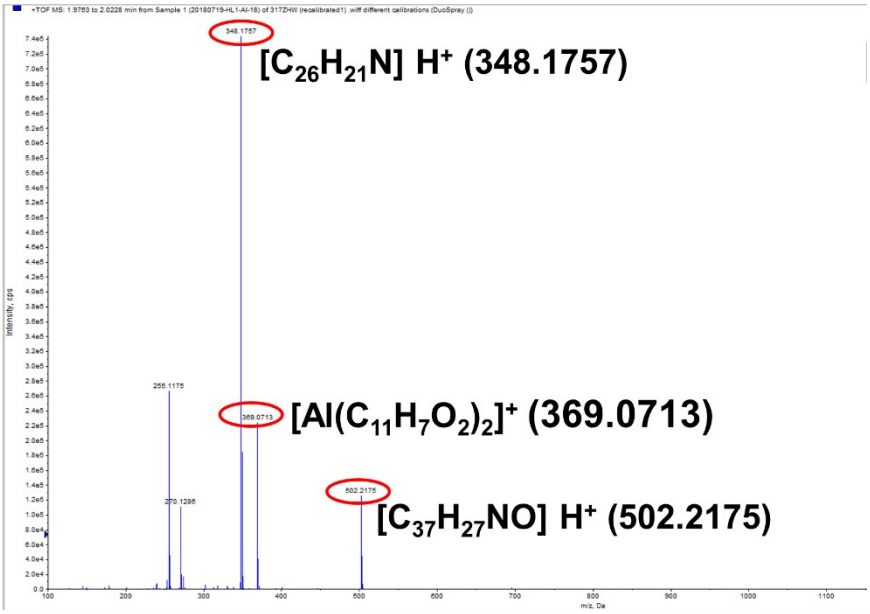
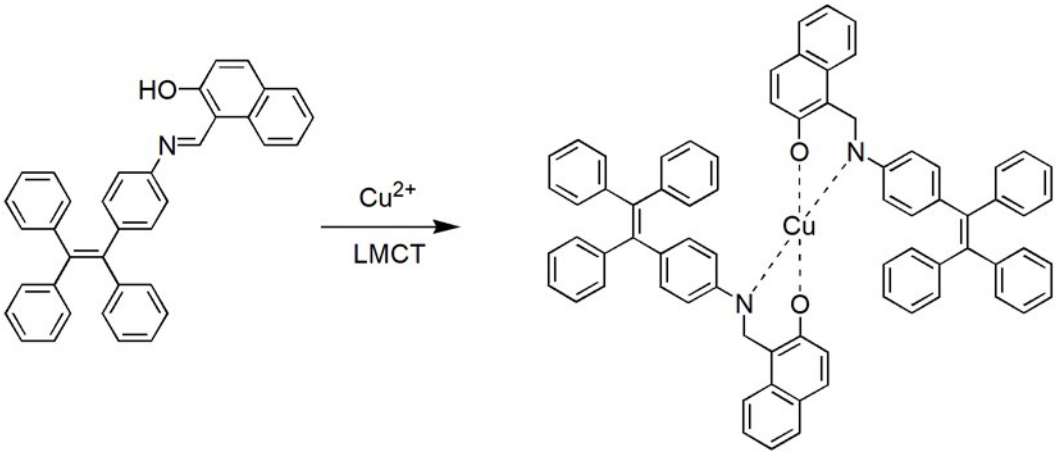
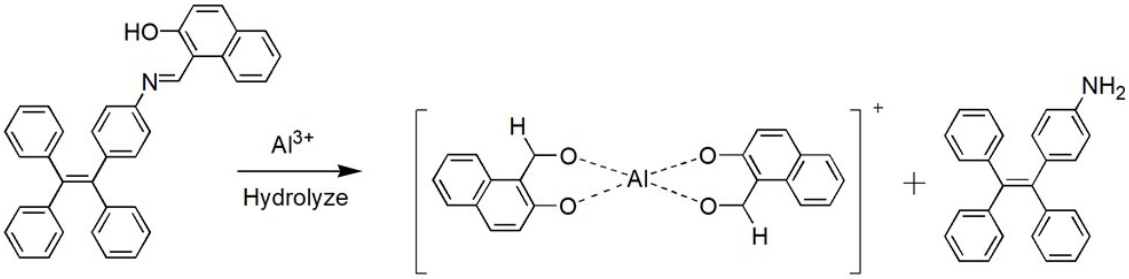


Figure S23. ESI-MS of HL (100μM) upon addition 1.0 equiv. of $Al(ClO_4)_3$ in ethanol.



Scheme S1. Possible species formed in detection of Cu^{2+} ion.



Scheme S2. Possible species formed in detection of Al^{3+} ion.

Table S1 Crystal data and structure refinement parameters of the tautomers of HL^e and HL^k.

Compound	**HL^k**	**HL^k-grinding**	**HL^e**	**HL^e-grinding**	**HL^k-fuming**
Formula	$C_{37}H_{27}NO$	$C_{37}H_{27}NO$	$C_{37}H_{27}NO$	$C_{37}H_{27}NO$	$C_{37}H_{27}NO$
Fw	501.59	501.59	501.59	501.59	501.59
T (K)	99.99(10)	100.00(10)	100.01(10)	99.99(10)	100.01(10)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.0127(2)	7.0152(3)	9.2313(4)	9.2294(4)	9.2297(7)
b (Å)	10.5362(3)	10.5390(4)	12.0971(6)	12.1005(5)	12.0832(9)
c (Å)	19.7029(7)	19.6920(7)	12.3074(6)	12.2959(4)	12.2987(8)
α (°)	74.751(3)	74.768(3)	83.688(4)	83.684(3)	83.780(6)
β (°)	87.075(3)	87.058(3)	70.851(4)	70.940(4)	70.829(6)
γ (°)	72.064(3)	71.880(3)	86.482(4)	86.467(4)	86.418(6)
V (Å^3)	1335.57(8)	1334.35(9)	1290.01(11)	1289.57(9)	1287.38(17)
Z	2	2	2	2	2
Calculated density (gcm^{-3})	1.247	1.248	1.291	1.292	1.294
F(000)	528.0	528.0	528.0	528.0	528.0
Reflections Collected/Unique	9049/5192	8899/5064	8745/4904	8751/4913	8758/4909
Goodness-of-fit on F^2	1.037	1.047	1.033	1.057	1.059
Final R indexes [I>=2σ(I)]	R1 =0.0371, wR2=0.0942	R1=0.0465, wR2=0.1191	R1 =0.0393, wR2 =0.0962	R1 =0.0660, wR2 =0.1769	R1 =0.0426 wR2 =0.1072
R indices (all data)	R1 =0.0426, wR2=0.0982	R1 =0.0653, wR2=0.1289	R1 =0.0462, wR2 =0.1013	R1 = 0.0920, wR2 =0.1903	R1 = 0.0531 wR2 =0.1124
CCDC number	1959911	1973185	1959912	1973186	1973187

Table S2. The optimized Cartesian Coordinates(in Å) of species studied.

Species	Cartesian coordinates				Species	Cartesian coordinates			
HL^e, ground state	C	6.72294	2.72986	-0.78948	HL^e, excited state	C	6.68203	2.76357	-0.78116
	H	6.40349	3.74674	-1.00353		H	6.35755	3.78956	-0.93464
	C	8.09904	2.41856	-0.77033		C	8.05117	2.44291	-0.83608
	H	8.83679	3.19107	-0.96906		H	8.78819	3.21730	-1.03122
	C	8.49294	1.12684	-0.49655		C	8.44577	1.13510	-0.64032
	H	9.54816	0.86291	-0.47555		H	9.49955	0.86734	-0.67968
	C	5.77137	1.76017	-0.53923		C	5.73884	1.77884	-0.53311
	C	6.13919	0.41789	-0.25415		C	6.10426	0.42845	-0.32503
	H	4.72628	2.04971	-0.56406		H	4.69407	2.06997	-0.50323
	C	5.18340	-0.63722	0.01299		C	5.13677	-0.63360	-0.06205
	C	7.53896	0.11106	-0.23550		C	7.50217	0.10874	-0.38422
	C	5.65999	-1.93734	0.29290		C	5.63543	-1.96478	0.13058
	C	3.75792	-0.38820	-0.00034		C	3.74587	-0.38085	0.01462
	C	7.95631	-1.22156	0.04865		C	7.92350	-1.23495	-0.18474
	O	4.84175	-2.96353	0.55845		O	4.81871	-2.99499	0.38652
	C	7.05194	-2.21583	0.30605		C	7.01410	-2.23974	0.06716
	N	2.88806	-1.31994	0.25073		N	2.85163	-1.33876	0.28546
	H	3.41527	0.62617	-0.21791		H	3.39864	0.64608	-0.10218
	H	9.02188	-1.44022	0.05972		H	8.98582	-1.46112	-0.23312
	H	3.89746	-2.60595	0.52091		H	3.87986	-2.62326	0.42552
	H	7.36431	-3.23239	0.52507		H	7.32858	-3.26688	0.22383
	C	1.50650	-1.07316	0.17441		C	1.50739	-1.11727	0.19738
	C	0.92613	-0.15745	-0.72208		C	0.90167	-0.06324	-0.55040
	C	0.65949	-1.82406	1.00674		C	0.63172	-2.01943	0.86803
	H	1.55042	0.38122	-1.42987		H	1.52484	0.59374	-1.14847
	C	-0.45205	0.02810	-0.74585		C	-0.46571	0.10333	-0.56750
	C	-0.71693	-1.63557	0.97325		C	-0.73509	-1.86404	0.82555
	H	1.10128	-2.54763	1.68652		H	1.07906	-2.82884	1.43755
	C	-1.30470	-0.69115	0.11073		C	-1.34414	-0.78267	0.11875
	H	-0.88068	0.73034	-1.45434		H	-0.89373	0.90666	-1.15926
	H	-1.35107	-2.22687	1.62795		H	-1.36383	-2.55251	1.38150
	C	-2.78696	-0.52396	0.05640		C	-2.77724	-0.57039	0.12313
	C	-3.56056	-1.80309	0.00157		C	-3.65784	-1.75239	0.19723
	C	-3.39151	0.70179	0.06015		C	-3.33964	0.74290	0.06350
	C	-3.20960	-2.81330	-0.91156		C	-3.32351	-2.95030	-0.47375
	C	-4.61515	-2.05392	0.89595		C	-4.84676	-1.73076	0.96011
	C	-4.83989	0.88845	-0.26004		C	-4.63514	0.97103	-0.59050
	C	-2.65694	1.96205	0.38876		C	-2.64409	1.89539	0.64824
	H	-2.38527	-2.64578	-1.59988		H	-2.42242	-2.98223	-1.07748
	C	-3.90937	-4.01887	-0.95104		C	-4.14824	-4.06813	-0.39556
	H	-4.88773	-1.29310	1.62140		H	-5.11270	-0.82659	1.49771
	C	-5.30773	-3.26421	0.86563		C	-5.66012	-2.85460	1.04940

	C	-5.65778	1.68120	0.56505		C	-5.55553	1.92683	-0.09292
	C	-5.40807	0.33176	-1.41889		C	-5.01095	0.24399	-1.74641
	C	-1.87860	2.06759	1.55442		C	-1.86595	1.76793	1.82754
	C	-2.77808	3.09646	-0.43369		C	-2.74574	3.18680	0.07234
	H	-3.62936	-4.78058	-1.67471		H	-3.88067	-4.97283	-0.93442
	C	-4.96177	-4.24987	-0.06160		C	-5.31781	-4.02717	0.36867
	H	-6.11622	-3.43885	1.57144		H	-6.56270	-2.81935	1.65320
	H	-5.23311	2.13550	1.45636		H	-5.30411	2.48629	0.80244
	C	-7.00338	1.88303	0.26007		C	-6.78500	2.12969	-0.70844
	H	-4.78756	-0.26667	-2.07926		H	-4.31604	-0.47556	-2.16634
	C	-6.75056	0.54381	-1.73169		C	-6.23671	0.45899	-2.36548
	H	-1.79063	1.20850	2.21303		H	-1.77604	0.79503	2.29846
	C	-1.22821	3.25864	1.87637		C	-1.23869	2.86734	2.39776
	H	-3.39092	3.04095	-1.32957		H	-3.31153	3.31352	-0.84495
	C	-2.11739	4.28366	-0.11967		C	-2.10293	4.28128	0.63924
	H	-5.50261	-5.19259	-0.08632		H	-5.95844	-4.90234	0.43329
	H	-7.62012	2.48830	0.92008		H	-7.47952	2.85535	-0.29355
	C	-7.55586	1.31554	-0.89088		C	-7.13357	1.39965	-1.85000
	H	-7.16668	0.10873	-2.63717		H	-6.49249	-0.10443	-3.25881
	H	-0.63746	3.31939	2.78724		H	-0.66042	2.74082	3.30895
	C	-1.33964	4.37021	1.03783		C	-1.34846	4.13145	1.80728
	H	-2.21439	5.14407	-0.77741		H	-2.18224	5.25524	0.16364
	H	-8.60277	1.47926	-1.13387		H	-8.09333	1.56301	-2.33225
	H	-0.83153	5.29815	1.28802		H	-0.84808	4.98804	2.25016
HL^k, ground state	C	-6.95532	2.27499	1.83242	HL^k, excited state	C	-6.95284	2.45198	1.61776
	H	-6.68288	3.13471	2.43873		H	-6.68746	3.37709	2.12305
	C	-8.30896	1.97275	1.61312		C	-8.30291	2.11473	1.42709
	H	-9.08836	2.59295	2.04587		H	-9.09017	2.77491	1.78105
	C	-8.63319	0.87288	0.83736		C	-8.61774	0.92912	0.78446
	H	-9.67426	0.61810	0.65284		H	-9.65839	0.65095	0.63038
	C	-5.95365	1.48757	1.28281		C	-5.95016	1.60672	1.16435
	C	-6.25251	0.35830	0.48669		C	-6.23627	0.39189	0.50149
	H	-4.92389	1.76481	1.48251		H	-4.92013	1.90349	1.33690
	C	-5.23717	-0.50803	-0.11682		C	-5.19882	-0.51813	0.00912
	C	-7.62997	0.05962	0.26980		C	-7.61507	0.05449	0.31568
	C	-5.63758	-1.65792	-0.93116		C	-5.60201	-1.77778	-0.66379
	C	-3.87773	-0.25344	0.07047		C	-3.85209	-0.21884	0.15282
	C	-7.98924	-1.08058	-0.53440		C	-7.96327	-1.17045	-0.34327
	O	-4.80341	-2.43425	-1.47787		O	-4.75315	-2.60760	-1.11113
	C	-7.06144	-1.89151	-1.10157		C	-7.01148	-2.03562	-0.80379
	N	-2.90017	-1.00008	-0.45342		N	-2.86222	-1.06237	-0.30347
	H	-3.55873	0.59385	0.66524		H	-3.52215	0.70088	0.61577
	H	-9.04883	-1.28131	-0.68053		H	-9.01942	-1.40021	-0.46948
	H	-3.26984	-1.78137	-1.02306		H	-3.28307	-1.90330	-0.75668

	H	-7.34304	-2.74808	-1.70672	H	-7.27707	-2.96330	-1.30212
	C	-1.51237	-0.83335	-0.31635	C	-1.51474	-0.91174	-0.20681
	C	-0.92654	0.12128	0.52950	C	-0.88639	0.17773	0.45968
	C	-0.68027	-1.68493	-1.06031	C	-0.67541	-1.89746	-0.80209
	H	-1.53563	0.77418	1.14553	H	-1.48400	0.92670	0.96636
	C	0.45793	0.22718	0.60333	C	0.48661	0.28104	0.49198
	C	0.70168	-1.57822	-0.96440	C	0.69399	-1.79509	-0.74036
	H	-1.12365	-2.43081	-1.71448	H	-1.13945	-2.73152	-1.32139
	C	1.30660	-0.60727	-0.14606	C	1.33922	-0.69193	-0.10221
	H	0.89227	0.96712	1.26752	H	0.93476	1.11491	1.02197
	H	1.32431	-2.25374	-1.54315	H	1.30020	-2.55178	-1.22778
	C	2.79153	-0.51903	-0.03126	C	2.78188	-0.55870	-0.07751
	C	3.48408	-1.83190	0.15459	C	3.58786	-1.79860	-0.03777
	C	3.46770	0.66698	-0.09427	C	3.42230	0.71354	-0.09872
	C	3.03671	-2.74627	1.12489	C	3.17951	-2.90382	0.74026
	C	4.55730	-2.21054	-0.67012	C	4.77065	-1.92381	-0.79778
	C	4.90838	0.79455	0.28378	C	4.73725	0.90673	0.53062
	C	2.82567	1.93792	-0.55048	C	2.79582	1.87395	-0.74763
	H	2.19751	-2.47938	1.76137	H	2.27920	-2.82258	1.34097
	C	3.66136	-3.98262	1.28692	C	3.93053	-4.07536	0.76833
	H	4.90350	-1.52574	-1.43822	H	5.09197	-1.09212	-1.41627
	C	5.17506	-3.45178	-0.51693	C	5.51034	-3.10126	-0.78061
	C	5.81043	1.47234	-0.55596	C	5.70682	1.76555	-0.04246
	C	5.38752	0.29643	1.50786	C	5.07735	0.25058	1.73796
	C	2.11138	1.99882	-1.75972	C	2.03185	1.73339	-1.93350
	C	2.97318	3.12188	0.19425	C	2.95966	3.18177	-0.22806
	H	3.30772	-4.66820	2.05252	H	3.60690	-4.90727	1.38769
	C	4.73352	-4.34105	0.46573	C	5.09687	-4.18075	0.00595
	H	5.99941	-3.72603	-1.16997	H	6.41039	-3.18041	-1.38403
	H	5.45619	1.88047	-1.49847	H	5.48007	2.27031	-0.97617
	C	7.15100	1.61731	-0.20012	C	6.95148	1.94196	0.55091
	H	4.70192	-0.21140	2.17917	H	4.34489	-0.39253	2.21418
	C	6.72538	0.45199	1.87038	C	6.31855	0.43968	2.33443
	H	2.00584	1.09996	-2.35954	H	1.90123	0.74637	-2.36391
	C	1.54669	3.19634	-2.19877	C	1.47041	2.83716	-2.56163
	H	3.53741	3.09978	1.12248	H	3.52254	3.31949	0.68955
	C	2.39819	4.31683	-0.23754	C	2.38229	4.28191	-0.85248
	H	5.21574	-5.30736	0.58605	H	5.67954	-5.09761	0.02378
	H	7.83324	2.13240	-0.87130	H	7.68382	2.59173	0.07928
	C	7.61458	1.10783	1.01559	C	7.26524	1.28245	1.74397
	H	7.07206	0.06407	2.82463	H	6.54780	-0.06677	3.26812
	H	1.00456	3.22143	-3.14042	H	0.90103	2.70078	-3.47690
	C	1.68240	4.35938	-1.43687	C	1.63692	4.11861	-2.02426
	H	2.51344	5.21668	0.36100	H	2.50723	5.27105	-0.42011

	H	8.65729	1.22724	1.29714		H	8.23672	1.42517	2.20895
	H	1.24117	5.29190	-1.77814		H	1.18859	4.97922	-2.51267

Table S3 Types of intermolecular interactions and corresponding bond distances and angles in HL^e and HL^k before and after grinding.

compound	interactions	Before grinding	After grinding
HL^e	C_{14}-$H_{14}\cdots O_1$	2.772 Å	2.761 Å
		126.79°	127.32°
	C_{34}-$H_{34}\cdots\pi$(C12-C17)	2.933 Å	2.929 Å
	C_{16}-$H_{16}\cdots\pi$(C4-C9)	161.71°	161.65°
		2.881 Å	2.867 Å
	$\pi\cdots\pi$ stacking	134.49°	135.29°
		3.459 Å	3.457 Å
HL^k	C_{14}-$H_{14}\cdots O_1$	2.568 Å	2.562 Å
		133.53°	134.11°
	C_2-$H_2\cdots\pi$(C19-C24)	3.322 Å	3.320 Å
		131.84°	131.34°

Table S4 Torsion angles before and after grinding.

tautomer	Torsion angles	Before grinding	After grinding
HL^e	N1-C11-C10-C1	-8.5 (2)	-9.0(3)
	C17-C12-N1-C11	-45.7(2)	-45.3(3)
	C25-C18-C15-C16	49.8(2)	50.6(3)
	C25-C18-C19-C24	55.5(2)	55.2(3)
	C33-C32-C25-C18	50.3(2)	50.1(3)
	C27-C26-C25-C18	51.8(2)	52.3(3)
HL^k	N1-C11-C10-C1	-4.1(2)	-4.1(2)
	C17-C12-N1-C11	14.7(2)	15.4(2)
	C25-C18-C15-C16	-45.0(2)	-44.7(2)
	C25-C18-C19-C24	-44.0(2)	-44.1(2)
	C33-C32-C25-C18	-46.5(2)	-46.3(2)
	C27-C26-C25-C18	-51.1(2)	-51.5(2)

Table S5 Binding energy(BE) for N 1s of HL^e and HL^k.

BE(eV)	HL^e	HL^e aggregates	HL^k	HL^k aggregates
N 1s	398.99	399.57	399.77	399.71