Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Strong and Insusceptible Photo-Emissions from An Intramolecular Weak Hydrogen Bonds Strengthened Twisted Fluorophore

Binhong Yu,[a] Danyang Liu,[a] Yi Wang,[a] Ting Zhang,[a] Yu-Mo Zhang,[b] Minjie Li*[a] and Sean Xiao-An Zhang*[a]

a B. Yu, D. Liu, Y. Wang, T. Zhang, Prof. M. Li, Prof. S. X.-A. Zhang
State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry
Jilin University
Changchun 130012, P. R. China
E-mail: liminjie@jlu.edu.cn, seanzhang@jlu.edu.cn

b Y.-M. Zhang
College of Chemistry
Jilin University
Changchun 130012, P. R. China

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Experimental Procedures

Instrument

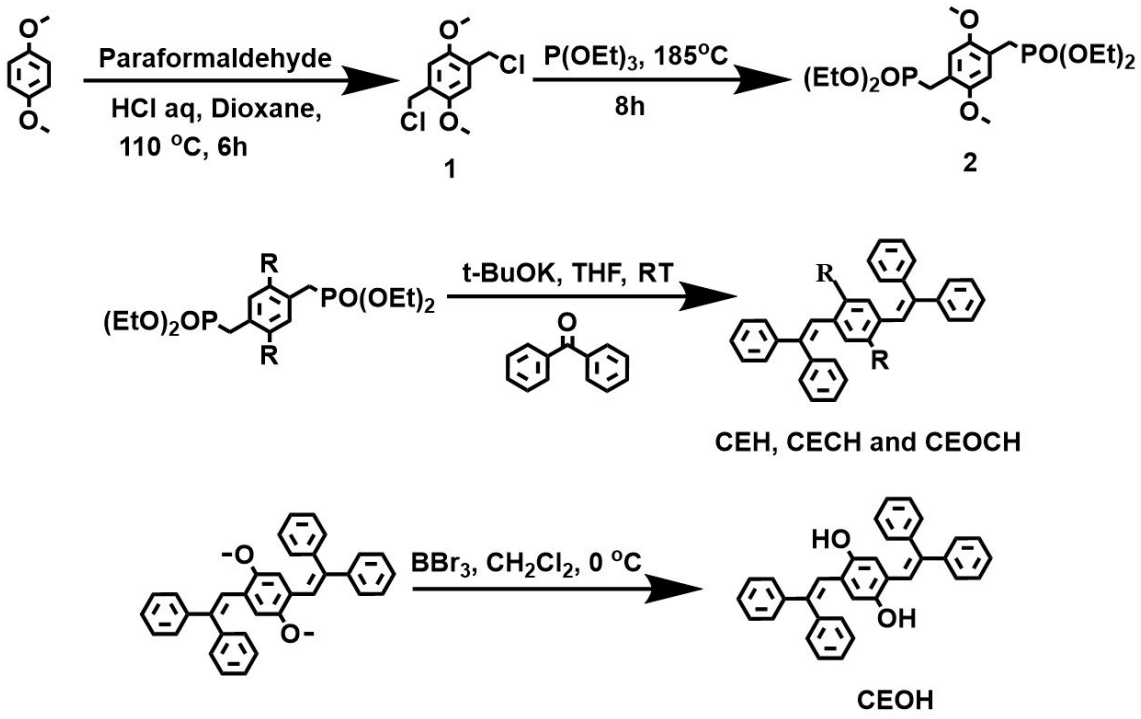
^{1}H NMR (500MHz) spectra and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE500 using CD_2CL_2, $CDCl_3$ or DMSO-D_6 with tetramethylsilane (TMS) at room temperature. Crystal data were recorded on a Rigaku R-AXIS RAPID. UV-Vis spectra of solutions were measured by an Analytikjena specord 2.10 plus. Fluorescence spectra were recorded by a Shimadzu RF-5301 PC spectrofluorimeter. The fluorescent quantum yield and life time were measured by Edinburgh Instrument LS920. Infra-red spectra (IR spectra) were recorded on a Brucker VERTEX 80V. Mass and melting points were tested by Thermo Fisher ITQ 1100 and NETZSCH DSC204, respectively. Images were taken by a Canon camera.

Materials

p-dimethoxybenzene, paraformaldehyde, triethyl phosphite, tetraethyl (1,4-phenylenebis(methylene))bis(phosphonate), tetraethyl ((2,5-dimethyl-1,4-phenylene)bis(methylene))bis(phosphonate), potassium tert-butylate, benzophenone, boron tribromide.
These materials were purchased commercially without purification and the solvents, such as THF and CH_2CL_2 were dried before using.

The Preparation of CEH, CECH, CEOH and CEOCH

Scheme S1. The syntheses of CEH, CECH, CEOH and CEOCH.



1,4-Bis(chloromethyl)-2,5-dimethoxybenzene[1] (1). Paraformaldehyde (0.80 g, 26.7 mmol) and p-dimethoxybenzene (1.39 g, 10.1 mmol) were added into round bottom flask with 20 ml 1,4-dioxane and 40 ml concentrated HCl solution. Firstly, the reaction was heated up to 80 °C for few minutes appearing white solid, and then increasing temperature to 110 °C for 6 h. Added large amount of water into reaction mixture and operated filtration to afford light yellow solid. The pure product (1), white solid was taken from the recrystallization in ethanol (yield: 1.25 g, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.93 (s, 2H), 4.64 (s, 4H), 3.86 (s, 6H).
Tetraethyl ((2,5-dimethoxy-1,4-phenylene)bis(methylene))bis(phosphonate)[1] (2). The product (2) came from the reaction mixing product (1) (1.0g, 4.27 mmol) and triethyl phosphit (1.8 ml, 10.4 mmol) in 185 °C for 8 h. Then, after pouring hexane to reaction system and taking ultrasonic, the white solid appeared and by filtration, the pure product (2) was gained (yield: 1.35 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.92 (s, 2H), 4.03 (p, *J*=7.0, 8H), 3.80 (s, 6H), 3.22 (d, *J*=20.3, 4H), 1.24 (t, *J*=7.0, 12H).
Products (CEH, CECH and CEOCH). The products (CEH, CECH and CEOCH) were from Witting Reaction (taking CEOCH as an example). Compound (2) (0.876 g, 2.0 mmol) and benzophenone (0.725 g, 3.98 mmol) were added in dry THF (20 ml) in Schelenk flask. Under nitrogen, we added potassium tert-butylate (0.896 g, 8.0 mmol) THF (8ml) solution slowly.[1] This reaction was carried out overnight. Then, adding saturated ammonium chloride aqueous solution into reaction system. The crude product was from the extraction by CH_2Cl_2 and after chromatography using petroleum ether/ CH_2Cl_2, the pure products were obtained. CEH (yield: 51%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 17H), 7.17 (dd, *J* = 7.1, 2.2 Hz, 4H), 6.86 (s, 2H), 6.79 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.50, 142.53, 140.40, 135.92, 130.39, 129.20, 128.65, 128.21, 127.91, 127.62, 127.50, 127.47; GCMS (EI): m/z calcd. [M]+ 434.20 found 434.53; melting point: 192.80 °C. CECH(yield: 48%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 16H), 7.21 – 7.12 (m, 4H), 6.94 (s, 2H), 6.63 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.70, 143.02, 140.45, 135.39, 133.58, 131.07, 130.69,

128.19, 128.07, 127.44, 127.12, 127.08, 19.55; GCMS (EI): m/z calcd. [M]+ 462.23 found 462.60; melting point: 205.62 °C. CEOCH (yield: 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.18 (m, 20H), 7.12 (s, 2H), 6.25 (s, 2H), 3.20 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.02, 143.49, 142.26, 141.01, 130.54, 128.68, 128.09, 127.71, 127.33, 127.24, 125.51, 122.37, 112.30, 55.25; GCMS (EI): m/z calcd. [M]+ 494.22 found 494.65; melting point: 245.73 °C.

Products (CEOH). CEOCH (0.189 g, 0.4 mmol) were added in dry CH_2Cl_2 (10 ml) in Schelenk flask at 0 °C. Then under nitrogen, BBr_3 (0.075 ml, 2.0 mmol) solution were added slowly.[2] This reaction was carried at 0 °C for 4 hours. Then, Na_2CO_3 aqueous solution was added to the mixture and the mixture was stirred for 1 hour. The mixture was extracted with CH_2Cl_2 and the organic layer was dried with Na_2SO_4. After removal of solvent, CEOH (0.099g, yield: 56%) was obtained as yellow solid. ^{1}H NMR (500 MHz, DMSO) δ 8.54 (s, 2H), 7.39 – 7.26 (m, 13H), 7.19 (d, *J* = 7.1 Hz, 4H), 7.11 (d, *J* = 6.8 Hz, 4H), 6.92 (s, 2H), 6.13 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.73, 144.31, 143.03, 139.62, 130.34, 128.61, 128.22, 128.04, 127.94, 127.82, 124.82, 122.29, 116.76; GCMS (EI): m/z calcd. [M]+ 466.19 found 466.48 melting point: 238.97 °C.

Crystal structure of CEH, CECH, CEOH and CEOCH

Table S1. Crystallographic Data for CEH, CECH, CEOH and CEOCH.

Crystal data				
CEH	CEH	CECH	CEOH	CEOCH
Chemical formula	$C_{34}H_{26}$	$C_{36}H_{30}$	$C_{36}H_{32}O_3$	$C_{36}H_{30}O_2$
M_r	434.55	462.6	512.61	494.6
Crystal system, space group	Triclinic, P^-1	Monoclinic, $P2_1/n$	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$
Temperature (K)	293	296	296	293
a, *b*, *c* (Å)	9.1613, 11.267, 13.686	9.0240, 8.3079, 17.6624	18.1516, 10.532, 28.615	15.885, 7.3696, 12.251
a, b, g (°)	103.00, 108.72, 103.56	90, 90.015, 90	90, 90, 90	90, 109.79, 90
V (Å^3)	1229.6 (4)	1324.16 (17)	5470.4 (8)	1349.5 (5)
Z	2	2	8	2
Radiation type	Mo *K*a	Mo *K*a	Mo *K*a	Mo *K*a
m (mm^{-1})	0.07	0.07	0.08	0.07
Crystal size (mm)	0.65 × 0.25 × 0.19	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18	0.61 × 0.39 × 0.15
Diffractometer	MoKa	CCD	CCD	MoKa
No. of measured, independent and observed [I > 2σ(I)] reflections	12115, 5571, 3387	8532, 2403, 1666	34882, 5049, 2295	12553, 3085, 2352
R_{int}	0.031	0.035	0.143	0.034
(sin q/l)$_{max}$ (Å^{-1})	0.649	0.602	0.604	0.649
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S*	0.048, 0.147, 1.00	0.051, 0.147, 1.04	0.060, 0.176, 0.93	0.044, 0.118, 1.07
No. of reflections	5571	2403	5049	3085
No. of parameters	307	164	356	174
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, -0.19	0.14, -0.20	0.24, -0.28	0.24, -0.19

Figure S1. Molecular structures of CEH (A), CECH (B), CEOH (C) and CEOCH (D).

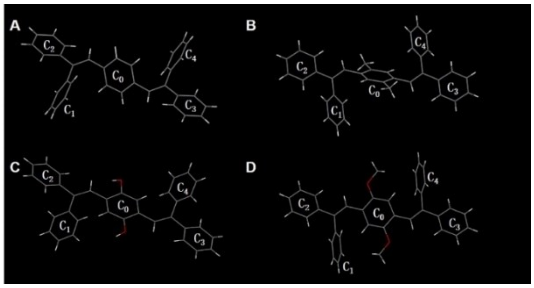
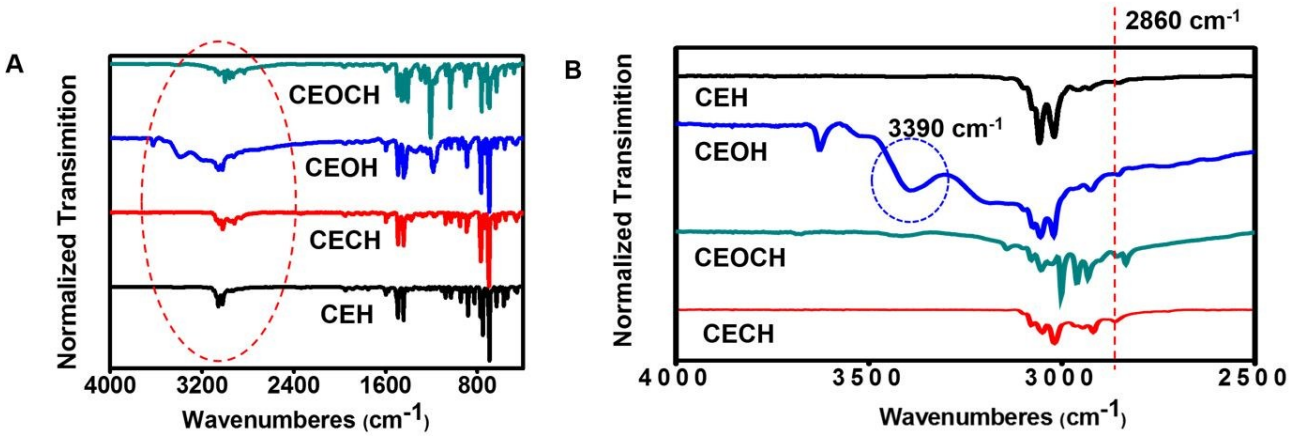


Table S2. The dihedral angles between central benzene ring and bordered benzene rings for each molecules.

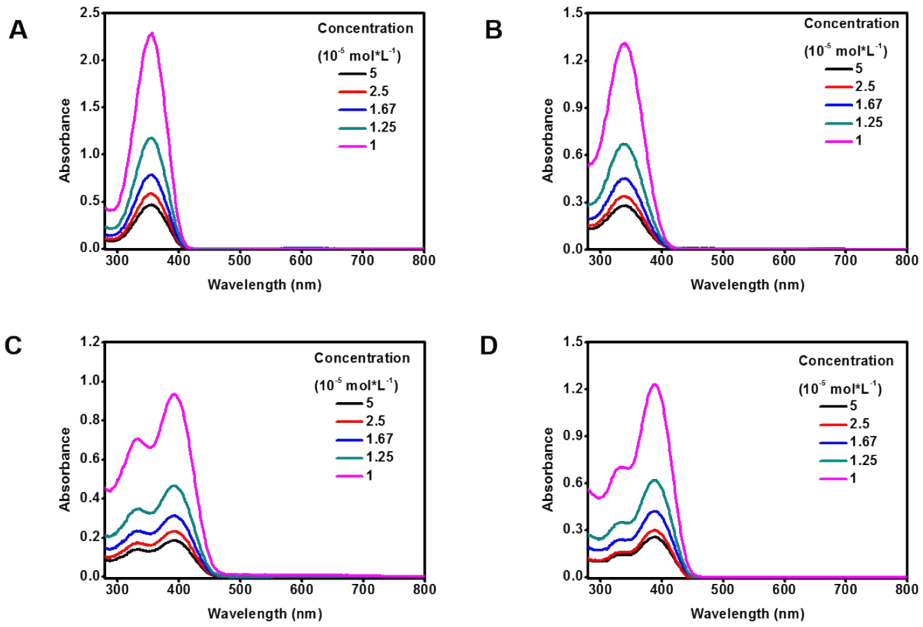
Molecules	Dihedral angels (°)			
	C_1-C_0	C_2-C_0	C_3-C_0	C_4-C_0
CEH	60.50	69.95	69.95	60.50
CECH	63.60	84.17	84.17	63.60
CEOH	55.15	83.74	76.25	57.97
CEOCH	77.55	32.09	32.09	77.55

Figure S2. FTIR spectra of CEH, CECH, CEOH and CEOCH.



The absorption spectra of CEH, CECH, CEOH and CEOCH with different concentrations

Figure S3. The absorption spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) with different concentrations (DMSO solution).



The absorption and emission spectra of CEH, CECH, CEOH and CEOCH in different aggregated states

Figure S4. Absorption spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in DMSO/water mixture solution (10 uM).

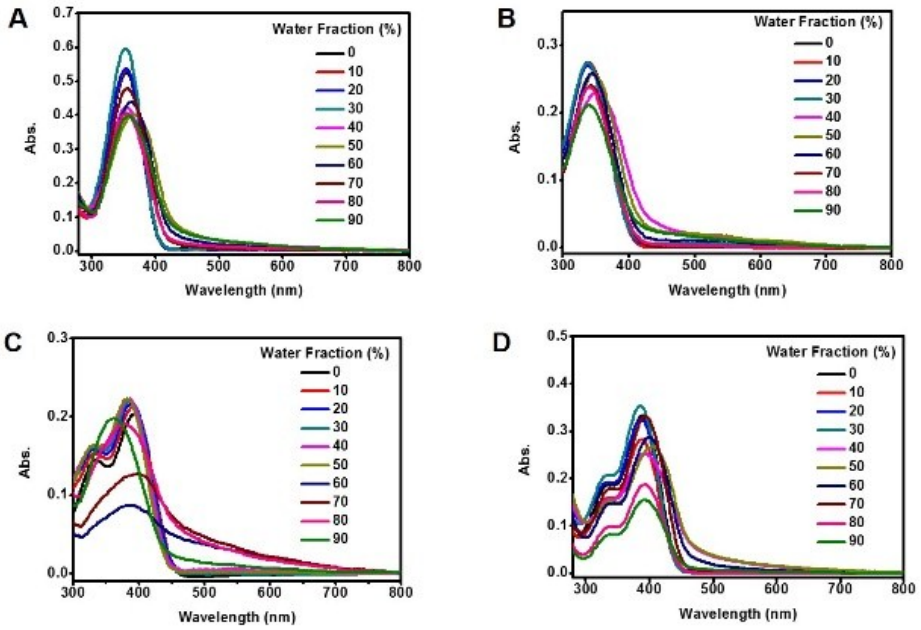
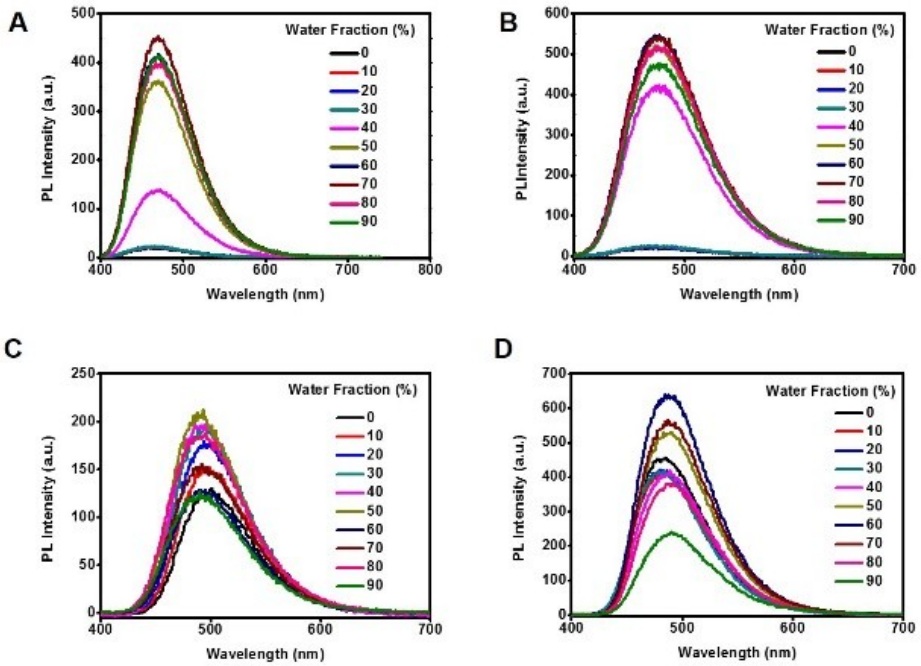


Figure S5. Emission spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in DMSO/water solution. Slits: 3, 1.5 for CEH and 1.5, 3 for CECH, CEOH and CEOCH. Excitation wavelength: 350 nm, 335 nm, 380 nm and 380 nm for CEH, CECH, CEOH and CEOCH.



The emissions of aggregation states and solid states show that CEH and CECH, whose fluorescent intensities have enhanced over 20 times during aggregated process exhibit traditional AIE phenomena because of the highly twisted bones and weak intermolecular forces, but CEOH and CEOCH display high emissions in both dissolved solution and aggregated states, which could be from the results of restriction of motions in unimolecular states or twisted structures and weak intermolecular forces in stacking.

Table S3. The average lifetimes (τ), quantum yields (ψ) and corresponding radiative (k_r) and nonradiative decay rates (k_{nr}) of CEOH and CEOCH as a function of water content.

Water fraction (%)	τ (ns)	ψ (%)	k_r ($10^8 s^{-1}$)	k_{nr} ($10^8 s^{-1}$)
		CEOH		
0	0.47	14.63	3.11	18.16
10	0.49	19.15	3.90	16.50

20	0.52	19.79	3.80	15.42
30	0.58	20.40	3.52	13.72
40	0.56	20.91	3.73	14.12
50	0.52	18.85	3.62	15.60
60	0.91	26.59	2.92	8.07
70	1.08	26.31	2.44	6.82
80	1.41	31.99	2.27	4.82
90	1.14	16.42	1.44	7.33
		CEOCH		
0	0.80	34.04	4.26	8.25
10	0.76	30.13	3.96	9.19
20	0.74	25.10	3.39	10.12
30	0.74	21.29	2.88	10.64
40	1.05	22.16	2.11	7.41
50	1.05	34.77	3.31	6.21
60	1.01	29.04	2.87	7.02
70	0.98	25.41	2.59	7.61
80	0.93	26.96	2.90	7.85
90	0.80	25.34	3.17	9.33

From the above results on the radiative and nonradiative rate constants as a function of the water content of CEOH and CEOCH, it is clear that the radiative and nonradiative rate constants of CEOH and CEOCH are influenced. When adding small amount of water (less than 40%), the values of k_{nr} of CEOH are gradually decreased, while the values of k_{nr} of CEOCH are gradually increased, indicating CEOH emits more strongly and CEOCH emits more weakly. When the water fraction continuously increased (higher than 50%), the aggregates formed.

The absorption and emission spectra of CEH, CECH, CEOH and CEOCH in different temperature and viscosity solutions

Figure S6. Absorption spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in different temperature (10 uM in DMSO).

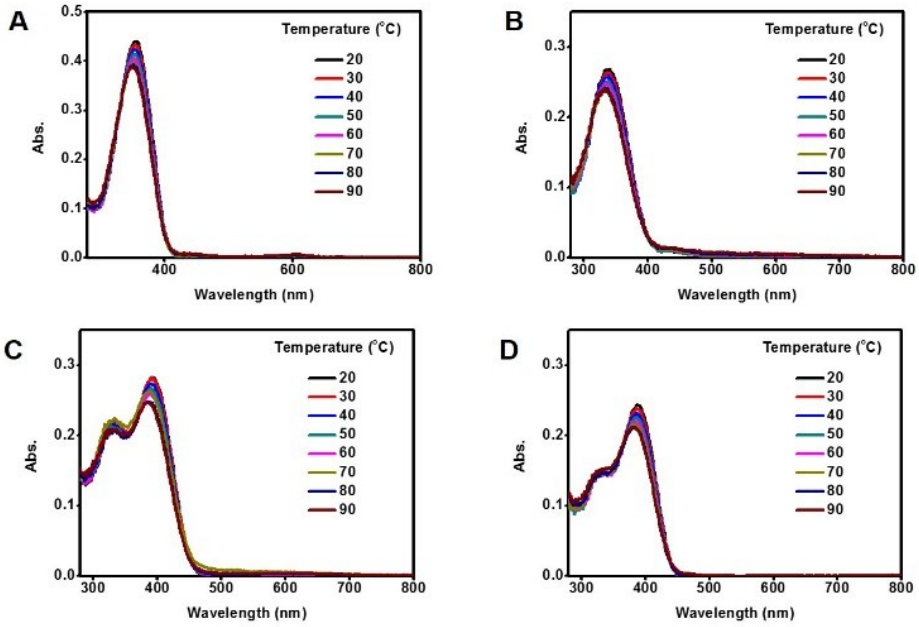


Figure S7. Emission spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in different temperature (10 uM in DMSO). Slits: 3, 5 for CEH and 5, 5 for CECH, 5, 3 for CEOH and 3, 3 for CEOCH. Excitation wavelength: 350 nm, 335 nm, 380 nm and 380 nm for CEH.CECH, CEOH and CEOCH.

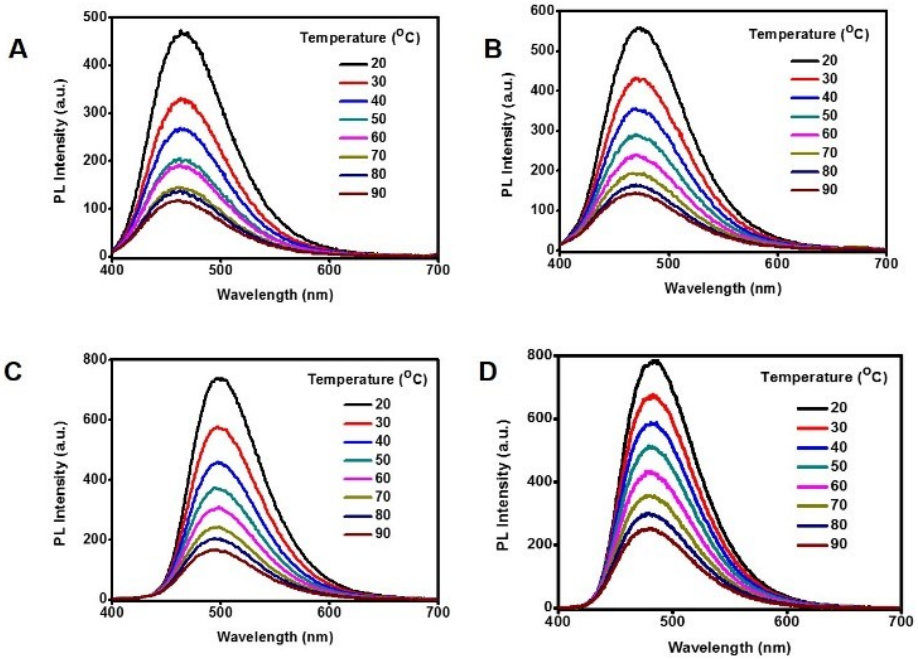


Figure S8. Absorption spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in different viscosity (10 uM in DMSO, MeOH and glycol mixture).

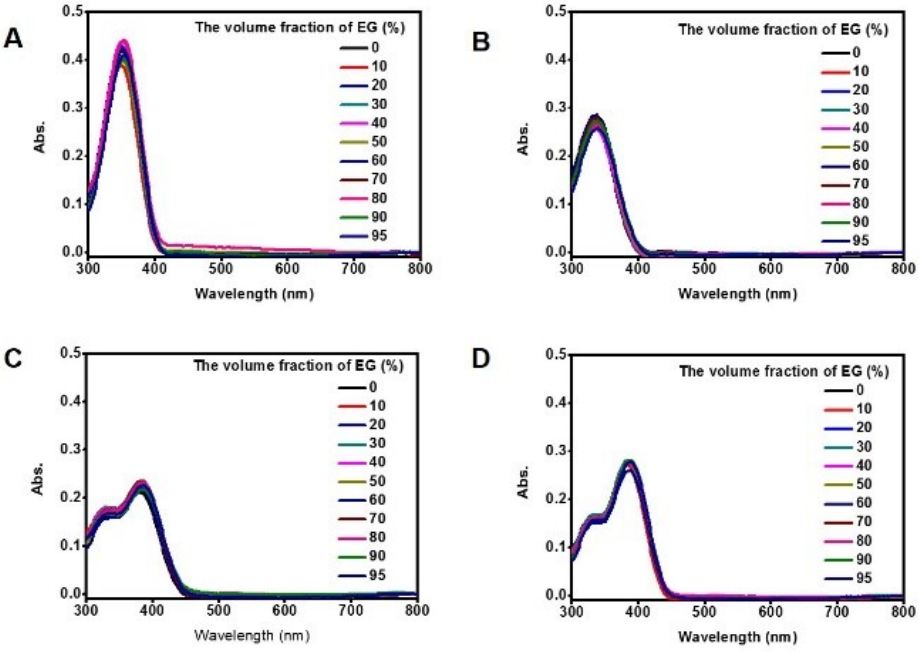
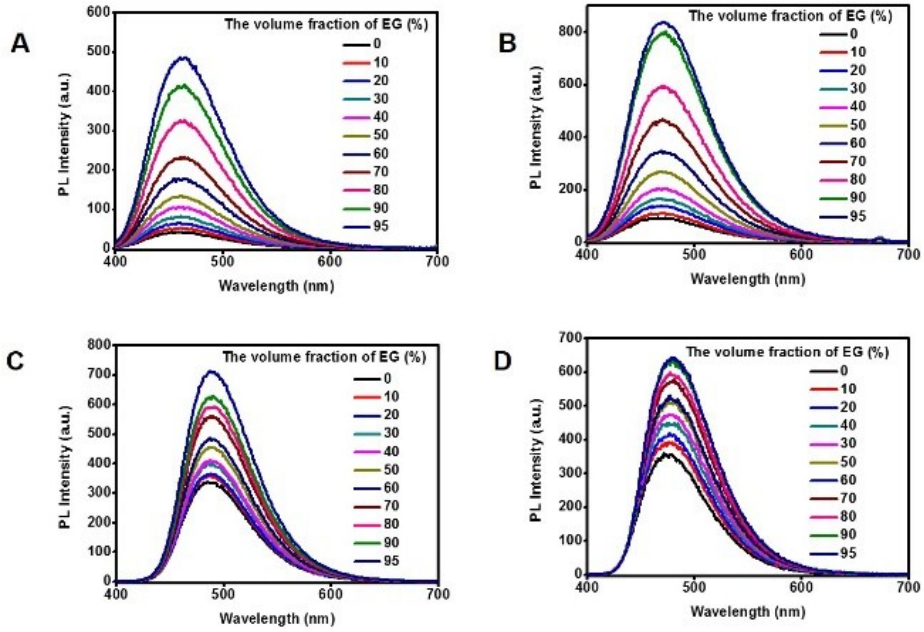


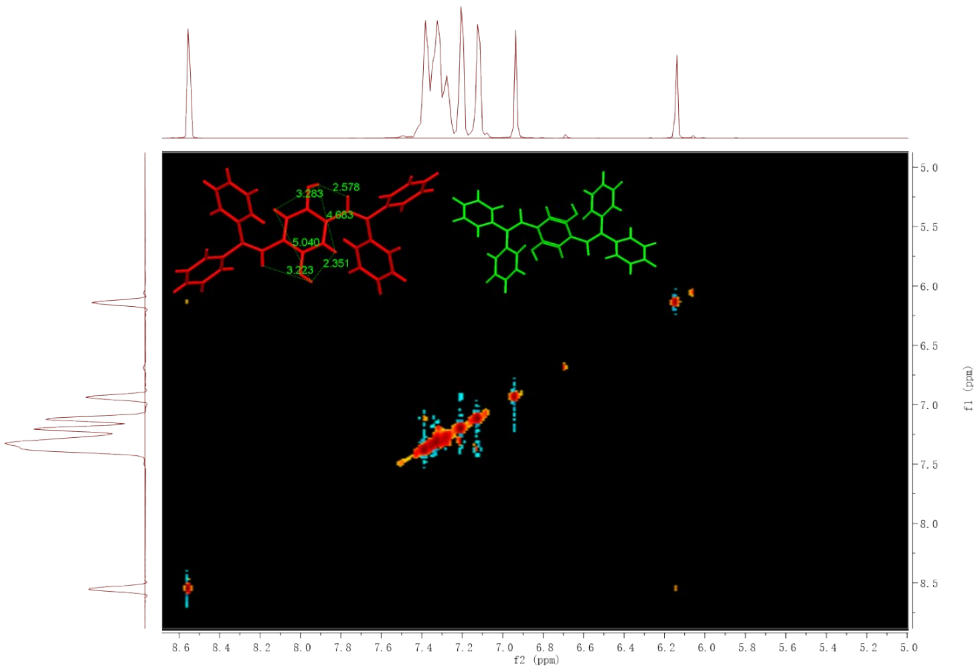
Figure S9. Emission spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in different viscosity (10 uM in DMSO, MeOH and glycol mixture). Slits: 3, 3 for CEH and 3, 5 for CECH, 3, 3 for CEOH and 1.5, 3 for CEOCH. Excitation wavelength: 350 nm, 335 nm, 380 nm and 380 nm for CEH.CECH, CEOH and CEOCH.



The absorption spectra of CEH, CECH, CEOH and CEOCH remain the same in different temperature and viscosity, but the emission intensities of these four molecules exhibit great enhancement when cooling down the temperature or increasing viscosity. The changes of temperature and viscosity are highly related to the molecular motions, which meant that the nonradiative pathways of these four molecules are mainly from rotations and vibrations.

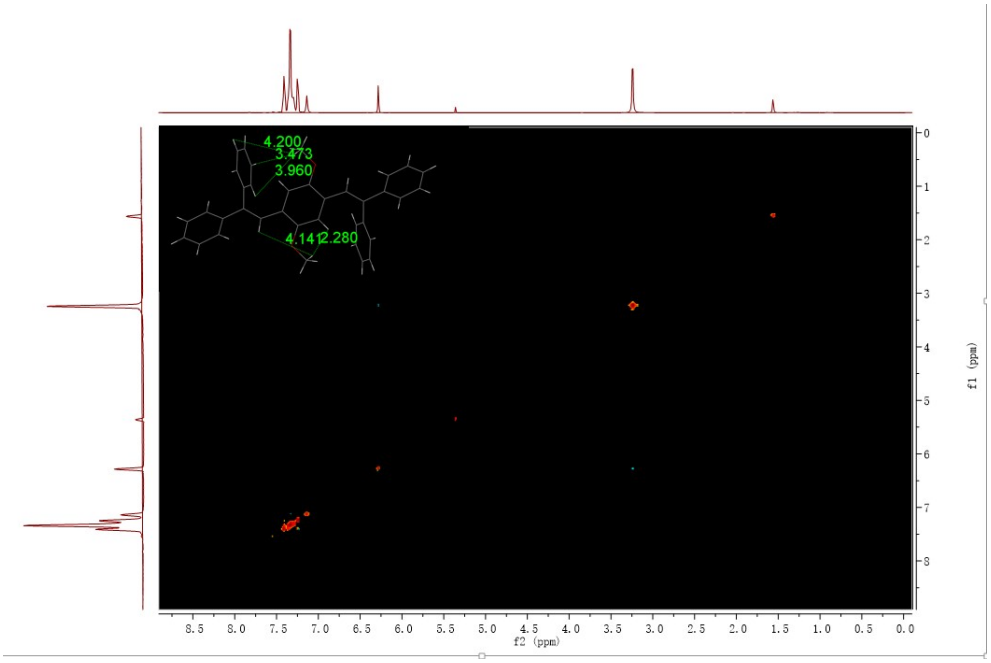
NOESY-NMR spectra of CEOH and CEOCH and VT-NMR spectra of CEOCH

Figure S10. NOESY-NMR spectra of CEOH in DMSO-D_6.



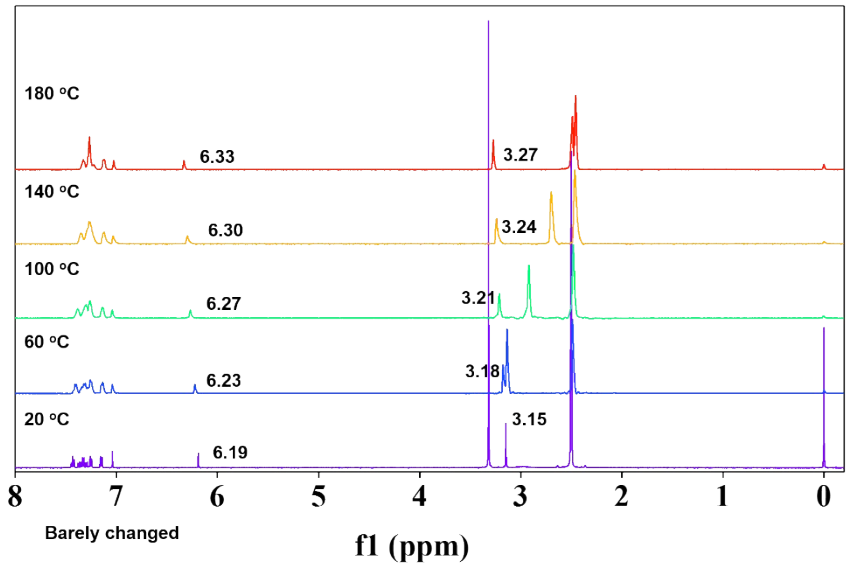
Because the unique peaks of hydrogens on central benzene rings, C=C double bonds and hydroxyl are not split in ^{1}H NMR spectrum of CEOH, its geometry would be symmetric (the green one) instead of asymmetric (the red one as in crystal) in solutions.

Figure S11. NOESY-NMR spectra of CEOCH in CD_2Cl_2.



In crystal structures of CEOH and CEOCH (inset images), the hydrogen atoms on –OH/-OCH_3 groups are spatially close to hydrogen atoms on benzene rings or C=C bonds. Thus, if IMWHBs are preserved in solution, the cross peaks will be detected by NOESY-NMR spectra. Fortunately, there are cross correlation peaks between –OH/-OCH_3 groups (8-9 ppm or 3-4 ppm) and central benzene rings/C=C bonds (6-7.15 ppm), which proves that the movements of –OH/-OCH_3 groups are limited and there are intramolecular CH…O interactions in CEOH and CEOCH. However, for the lack of cross correlation peaks between -OCH_3 groups (3-4 ppm) and bordered benzene rings (>7 ppm), the intramolecular CH/Pi interactions can't be deduced.

Figure S12. VT ^{1}H NMR spectra of CEOCH in DMSO.



^{1}H chemical shifts of methoxyl groups and central benzene result in upfield when temperature decreases, indicating the existence of IMWHBs, while the rest of spectra don't change with temperature basically.

Crystal structure of the oxidized product of CEOH

Figure S13. The oxidized product of CEOH during the cultivation process.

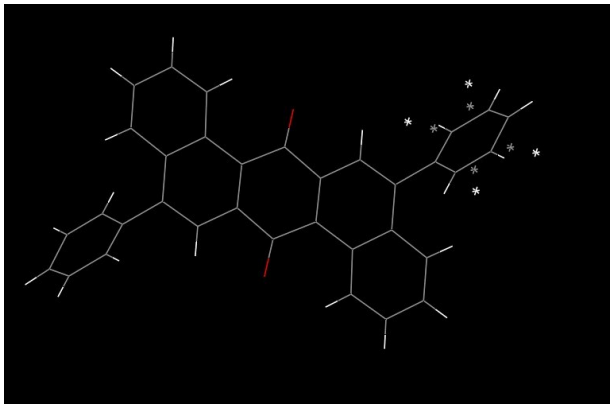


Table S4. Crystallographic Data for The oxidized products of CEOH.

Crystal data	
Oxidized CEOH	
Chemical formula	$C_{34}H_{20}O_2$
M_r	460.5
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, *b*, *c* (Å)	28.335, 5.014, 19.700
b (°)	90, 125.34, 90
V (Å^3)	2283.0 (18)
Z	4
Radiation type	Mo *K*a
m (mm^{-1})	0.08
Crystal size (mm)	0.22 × 0.20 × 0.18
Diffractometer	CCD
No. of measured, independent and observed [I > 2σ(I)] reflections	6975, 2074, 1106
R_{int}	0.081
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.605
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S*	0.083, 0.284, 0.99
No. of reflections	2074
No. of parameters	200
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, -0.30

The absorption and emission spectra of CEH, CECH, CEOH and CEOCH in different solvents

Figure S14. Absorption spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in different solvents (10 uM).

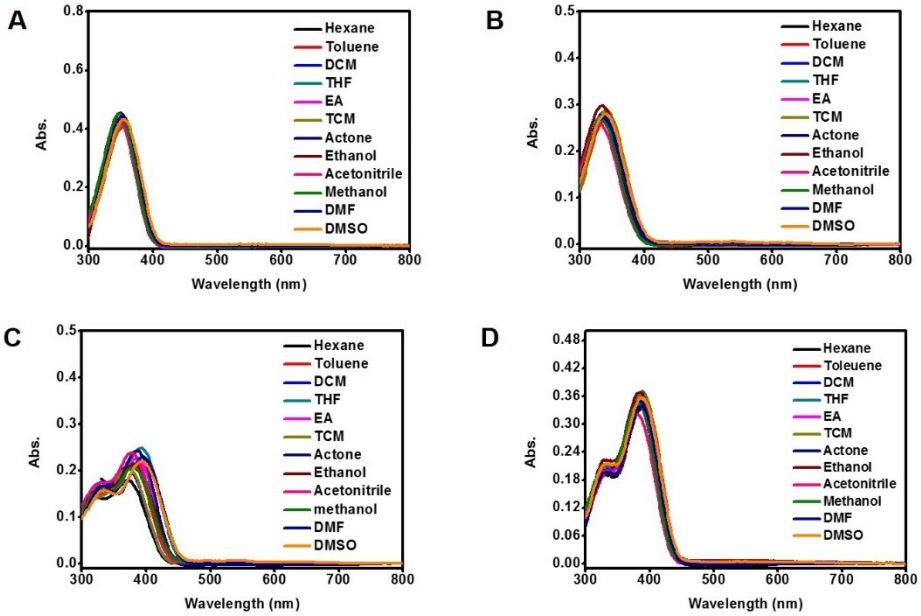
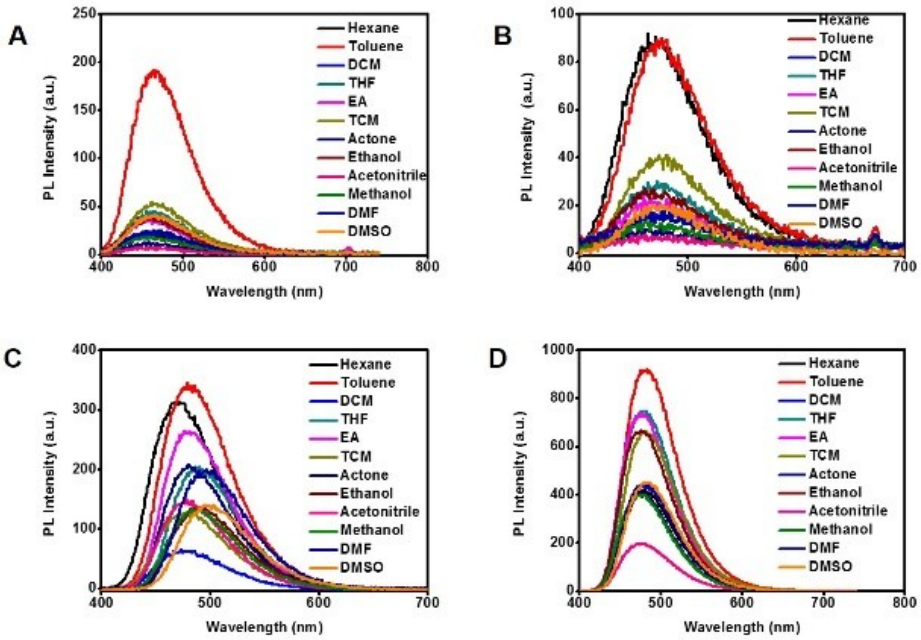


Figure S15. Emission spectra of CEH (A), CECH (B), CEOH (C) and CEOCH (D) in different temperature (10 uM in DMSO). Slits: 3, 5 for CEH and 5, 5 for CECH, 5, 3 for CEOH and 3, 3 for CEOCH. Excitation wavelength: 350 nm, 335 nm, 380 nm and 380 nm for CEH, CECH, CEOH and CEOCH.



The absorption and emission spectra of these four molecules change a little in different polarity and no matter if the solvent could break the hydrogen bonds, the emission intensities of CEOH and CEOCH are much stronger than CEH's and CECH's, which meant that the introducing donating groups have influenced the molecular HOMOs and LUMOs orbitals little and because IMWHBs come from dispersion force, the violent emission of CEOH and CEOCH could remain in hydrogen bond breaking agents, such as DMSO, DMF and MeOH and so on.

Calculation of CEH, CECH, CEOH and CEOCH

The optimization of ground states[3] and excited states[3] of CEH, CECH, CEOH and CEOCH were calculated based on B3LYP/6-31G(d,p) level, Gaussian 09 Program. On the optimized geometry of the ground state and the excited state, the first single excited states[3] and single point energies[3] of CEH,

CECH, CEOH and CEOCH were carried out with B3LYP/6-31G(d,p) level, Gaussian 09 Program.

Table S5. Calculated absorption and emission data for CEH, CECH, CEOH and CEOCH based on B3LYP/6-31G(d,p) level, Gaussian 09 Program.

	Absorption		Emission	
	Electronic state transition	Vertical excitation energy (nm)	Electronic state transition	Vertical excitation energy (nm)
CEH	$S_0 \rightarrow S_1$	391	$S_1 \rightarrow S_0$	524
CECH	$S_0 \rightarrow S_1$	384	$S_1 \rightarrow S_0$	533
CEOH	$S_0 \rightarrow S_1$	393	$S_1 \rightarrow S_0$	518
CEOCH	$S_0 \rightarrow S_1$	421	$S_1 \rightarrow S_0$	539

The calculated absorption and emission peaks of these molecules by B3LYP/6-31G (d,p) level (Table S6) fit well with the experimental data, which proves the reliability of calculated results.

Table S6. Calculated coordinate of CEH in the ground state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program.

Atom	x	y	z
C	-5.21982	-0.93702	0.045024
C	-4.05435	1.31784	0.001602
C	-0.37167	-1.136	0.693778
H	-0.65778	-2.02695	1.247342
C	0.968565	-0.78126	0.63075
H	1.703637	-1.39053	1.142444
C	-3.9435	-0.17023	0.056644
C	-1.37911	-0.36537	0.077322
C	-2.76525	-0.83829	0.16561
H	-2.84264	-1.90773	0.354377
C	-5.30954	-2.19549	-0.57824
H	-4.44609	-2.58898	-1.10551
C	-6.37459	-0.42585	0.666136
H	-6.33304	0.546287	1.146519
C	-4.75339	1.946986	-1.04209
H	-5.201	1.339446	-1.82305
C	-3.50202	2.119015	1.014221
H	-2.9728	1.643654	1.833993
C	-7.62793	-2.41057	0.077621
H	-8.5549	-2.97633	0.088873
C	-6.49662	-2.92502	-0.55798
H	-6.54176	-3.89092	-1.05317
C	-4.30887	4.120883	-0.07875
H	-4.40595	5.202184	-0.11016
C	-7.56074	-1.1563	0.687287
H	-8.43526	-0.74491	1.183408
C	-3.62857	3.506931	0.974618
H	-3.19795	4.109126	1.769543
C	-4.87074	3.335794	-1.08735
H	-5.40519	3.804529	-1.90873
C	5.219835	0.93701	-0.04505
C	4.054338	-1.31783	-0.00158
C	0.37168	1.136018	-0.6938
H	0.657797	2.026966	-1.24737
C	-0.96855	0.781279	-0.63078
H	-1.70362	1.390555	-1.14247
C	3.943512	0.17024	-0.05666

C	1.379124	0.365393	-0.07735
C	2.765269	0.838308	-0.16563
H	2.842662	1.907746	-0.35441
C	5.309573	2.195499	0.578192
H	4.446124	2.589005	1.105449
C	6.374605	0.425813	-0.66615
H	6.333039	-0.54633	-1.14651
C	4.753383	-1.94696	1.042116
H	5.201015	-1.33941	1.823054
C	3.501978	-2.11902	-1.01417
H	2.972752	-1.64367	-1.83394
C	7.627964	2.410532	-0.07767
H	8.554945	2.97628	-0.08893
C	6.496664	2.925011	0.557915
H	6.541813	3.890916	1.053081
C	4.308811	-4.12088	0.07884
H	4.405869	-5.20218	0.110267
C	7.560765	1.15625	-0.68731
H	8.435273	0.744836	-1.18342
C	3.628504	-3.50694	-0.97454
H	3.197859	-4.10915	-1.76944
C	4.870711	-3.33577	1.087405
H	5.405168	-3.8045	1.908789

Table S7. Calculated coordinate of CEH in the excited state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program.

Atom	x	y	z
C	5.16868	0.922847	0.069645
C	4.060715	-1.35422	0.078141
C	0.331079	1.116541	0.761204
H	0.59694	1.973766	1.374829
C	-0.99258	0.792352	0.600583
H	-1.74968	1.380757	1.102276
C	3.949913	0.107499	0.158128
C	1.388726	0.344781	0.187184
C	2.731868	0.766874	0.395121
H	2.821098	1.780676	0.782585
C	5.123249	2.250755	-0.42025
H	4.185139	2.640063	-0.80273
C	6.4241	0.436688	0.509192
H	6.489736	-0.56727	0.914279
C	4.947217	-1.97863	-0.83238
H	5.541403	-1.35956	-1.49661
C	3.287135	-2.19398	0.917809
H	2.623693	-1.73987	1.64551
C	7.491547	2.544748	-0.01884
H	8.381567	3.16613	-0.05146
C	6.263964	3.044994	-0.46198
H	6.198869	4.056307	-0.85392
C	4.266126	-4.17391	-0.07103
H	4.344145	-5.25544	-0.13068
C	7.561407	1.234473	0.465932
H	8.507345	0.837609	0.82386
C	3.394236	-3.57871	0.844523

H	2.798932	-4.19782	1.509874
C	5.040823	-3.36315	-0.90969
H	5.715384	-3.81579	-1.63104
C	-5.16869	-0.92284	-0.06967
C	-4.06071	1.35422	-0.07812
C	-0.33109	-1.11655	-0.76123
H	-0.59695	-1.97377	-1.37486
C	0.992563	-0.79236	-0.60061
H	1.749663	-1.38076	-1.10231
C	-3.94992	-0.1075	-0.15814
C	-1.38874	-0.34479	-0.18721
C	-2.73188	-0.76688	-0.39515
H	-2.82112	-1.78067	-0.78263
C	-5.12327	-2.25076	0.420216
H	-4.18516	-2.64007	0.802692
C	-6.42411	-0.43668	-0.50921
H	-6.48974	0.567289	-0.91429
C	-4.94721	1.978616	0.832413
H	-5.5414	1.359546	1.496623
C	-3.28711	2.193983	-0.91777
H	-2.62367	1.739877	-1.64547
C	-7.49157	-2.54474	0.018797
H	-8.38159	-3.16612	0.051405
C	-6.26399	-3.04499	0.461932
H	-6.1989	-4.05631	0.853868
C	-4.26608	4.17391	0.071111
H	-4.34409	5.255434	0.130785
C	-7.56142	-1.23446	-0.46596
H	-8.50736	-0.83759	-0.82389
C	-3.3942	3.578712	-0.84445
H	-2.79888	4.197832	-1.50979
C	-5.04079	3.363134	0.909748
H	-5.71535	3.815777	1.6311

Table S8. Calculated coordinate of CECH in the ground state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program.

Atom	x	y	z
C	5.32707	2.063693	-0.77036
H	4.469174	2.431473	-1.32468
C	6.53389	2.758869	-0.82408
H	6.601175	3.674107	-1.40552
C	7.655752	2.273508	-0.15034
H	8.597849	2.811904	-0.19641
C	7.559469	1.083047	0.572955
H	8.426313	0.695167	1.100497
C	6.353701	0.386999	0.62544
H	6.289172	-0.53551	1.193301
C	5.208819	0.870469	-0.03446
C	3.909814	0.146981	0.056547
C	3.968239	-1.34396	0.104966
C	4.701861	-2.06364	-0.85362
H	5.217827	-1.52385	-1.64206
C	4.767383	-3.45571	-0.8066
H	5.330815	-3.99402	-1.56348

C	4.116511	-4.15496	0.211382
H	4.173115	-5.23884	0.252673
C	3.399842	-3.45123	1.181305
H	2.900391	-3.98605	1.984169
C	3.32604	-2.06037	1.128488
H	2.769935	-1.51637	1.884977
C	2.756261	0.859745	0.139099
H	2.873291	1.936022	0.248467
C	1.359357	0.400706	0.09283
C	0.368684	1.072401	0.850887
C	0.722969	2.208865	1.781853
H	-0.15321	2.53475	2.348021
H	1.100476	3.081449	1.233483
H	1.502657	1.923328	2.496312
C	-0.95539	0.651786	0.746414
H	-1.70657	1.149036	1.351085
C	-5.32719	-2.06378	0.77002
H	-4.46931	-2.43169	1.324292
C	-6.53404	-2.75891	0.823641
H	-6.60137	-3.67424	1.40494
C	-7.65588	-2.2734	0.14997
H	-8.598	-2.81176	0.195961
C	-7.55954	-1.08283	-0.57314
H	-8.42637	-0.69483	-1.10063
C	-6.35374	-0.38683	-0.62552
H	-6.28917	0.535763	-1.19324
C	-5.20889	-0.87045	0.034307
C	-3.90985	-0.14701	-0.05659
C	-3.96819	1.343932	-0.10479
C	-4.70182	2.063523	0.853859
H	-5.21787	1.523642	1.642191
C	-4.76725	3.455597	0.807043
H	-5.33069	3.993831	1.563972
C	-4.11627	4.154955	-0.21079
H	-4.1728	5.238848	-0.25193
C	-3.39958	3.451329	-1.18077
H	-2.90003	3.986234	-1.98352
C	-3.32587	2.060457	-1.12816
H	-2.76974	1.51653	-1.88469
C	-2.75632	-0.85981	-0.13922
H	-2.87337	-1.93607	-0.24865
C	-1.35941	-0.40078	-0.09296
C	-0.36875	-1.07246	-0.85103
C	-0.72303	-2.20891	-1.78202
H	0.15314	-2.53478	-2.34819
H	-1.10054	-3.0815	-1.23366
H	-1.50273	-1.92336	-2.49647
C	0.955327	-0.65185	-0.74656
H	1.706501	-1.14909	-1.35124

Table S9. Calculated coordinate of CECH in the excited state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program.

Atom	x	y	z
C	5.128178	-2.17273	0.580296

H	4.191269	-2.55191	0.975941
C	6.28179	-2.94156	0.690975
H	6.228641	-3.9248	1.150448
C	7.506667	-2.45055	0.230588
H	8.40681	-3.05183	0.317462
C	7.560427	-1.17552	-0.34219
H	8.504207	-0.78679	-0.71451
C	6.410038	-0.4034	-0.45452
H	6.464157	0.571505	-0.9268
C	5.157362	-0.88059	0.001786
C	3.924675	-0.09616	-0.15639
C	4.008799	1.369637	-0.16947
C	4.880525	2.067258	0.701311
H	5.484222	1.503489	1.405024
C	4.94851	3.455627	0.691538
H	5.613294	3.964625	1.383883
C	4.161354	4.19786	-0.19702
H	4.219342	5.282252	-0.20573
C	3.302436	3.529445	-1.07373
H	2.696891	4.093997	-1.77735
C	3.221305	2.141308	-1.05998
H	2.566768	1.631048	-1.75786
C	2.724595	-0.79587	-0.37421
H	2.854294	-1.82435	-0.69946
C	1.370999	-0.38602	-0.20228
C	0.300876	-1.15364	-0.78649
C	0.585972	-2.35701	-1.65201
H	-0.34121	-2.76823	-2.05828
H	1.079375	-3.15691	-1.08552
H	1.246593	-2.10864	-2.49047
C	-1.00129	-0.75595	-0.58613
H	-1.78987	-1.30694	-1.08341
C	-5.12828	2.172662	-0.58038
H	-4.19141	2.551781	-0.97617
C	-6.28189	2.941499	-0.69102
H	-6.22877	3.92469	-1.15061
C	-7.50673	2.450569	-0.23045
H	-8.40687	3.051853	-0.3173
C	-7.56045	1.175603	0.342474
H	-8.5042	0.786934	0.714948
C	-6.41007	0.403474	0.454769
H	-6.46416	-0.57137	0.927188
C	-5.15743	0.88058	-0.00173
C	-3.92473	0.096151	0.156409
C	-4.00878	-1.36965	0.169407
C	-4.88031	-2.06728	-0.70156
H	-5.48393	-1.50352	-1.40535
C	-4.9482	-3.45566	-0.69188
H	-5.61284	-3.96466	-1.38436
C	-4.16114	-4.19789	0.196765
H	-4.21905	-5.28228	0.2054
C	-3.3024	-3.52946	1.073637
H	-2.69691	-4.09401	1.777315

C	-3.22136	-2.14132	1.059978
H	-2.56696	-1.63105	1.757981
C	-2.72466	0.795874	0.37428
H	-2.85437	1.824331	0.699591
C	-1.37106	0.386042	0.202346
C	-0.30094	1.153658	0.786559
C	-0.58604	2.357027	1.652082
H	0.341148	2.768249	2.058354
H	-1.07944	3.156933	1.0856
H	-1.24666	2.108657	2.490547
C	1.001219	0.755969	0.586202
H	1.789799	1.306959	1.08349

Table S10. Calculated coordinate of CEOH in the ground state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program

Atom	x	y	z
C	0.425547	0.927718	-0.91806
C	1.37939	0.382978	-0.04135
C	0.916173	-0.55325	0.907746
C	-0.42558	-0.92779	0.918139
C	-1.37942	-0.38305	0.041436
C	-0.91621	0.553178	-0.90767
C	-2.76711	-0.86946	0.118049
C	2.767067	0.869417	-0.11797
C	-3.93634	-0.18289	0.064172
C	-5.218	-0.94241	0.055788
C	-4.02325	1.303994	0.081349
C	3.936321	0.182881	-0.06414
C	5.217965	0.942436	-0.05574
C	4.02328	-1.304	-0.0814
C	6.336003	0.484956	-0.77686
C	7.520878	1.217601	-0.80271
C	7.622256	2.419766	-0.09962
C	6.527392	2.879779	0.633625
C	5.341402	2.147742	0.658559
C	3.291553	-2.05784	-1.01265
C	3.387803	-3.44878	-1.03984
C	4.219451	-4.11345	-0.13741
C	4.960792	-3.37498	0.787803
C	4.869339	-1.98492	0.810014
C	-4.86928	1.984892	-0.81011
C	-4.96069	3.37496	-0.78798
C	-4.21932	4.113455	0.137174
C	-3.38769	3.448816	1.039647
C	-3.29149	2.057869	1.012547
C	-6.33605	-0.48486	0.776856
C	-7.52094	-1.21748	0.802729
C	-7.62232	-2.41969	0.099709
C	-6.52745	-2.87977	-0.63348
C	-5.34145	-2.14776	-0.65843
O	-1.80462	1.039302	-1.82718
O	1.80458	-1.03938	1.827259

H	0.763744	1.648332	-1.6609
H	-0.76378	-1.6484	1.660985
H	-2.84589	-1.94437	0.274758
H	2.845815	1.94433	-0.27465
H	6.266168	-0.4461	-1.32997
H	8.367111	0.849416	-1.37592
H	8.548393	2.986916	-0.11526
H	6.600409	3.804064	1.1999
H	4.505408	2.494566	1.25793
H	2.650911	-1.54551	-1.72284
H	2.817974	-4.01295	-1.77287
H	4.296475	-5.19677	-0.16007
H	5.613929	-3.88292	1.491952
H	5.448962	-1.41571	1.530029
H	-5.44893	1.415653	-1.53008
H	-5.61381	3.882869	-1.49216
H	-4.2963	5.196779	0.159763
H	-2.81784	4.01301	1.772639
H	-2.65087	1.54557	1.722775
H	-6.26621	0.446229	1.329907
H	-8.36718	-0.84924	1.37589
H	-8.54847	-2.98682	0.115359
H	-6.60047	-3.80409	-1.1997
H	-4.50544	-2.49464	-1.25776
H	-1.36641	1.71662	-2.35803
H	1.36637	-1.71669	2.358108

Table S11. Calculated coordinate of CEOH in the excited state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program

Atom	x	y	z
C	0.367414	0.997803	-0.89111
C	1.398535	0.396798	-0.12503
C	0.957282	-0.60461	0.821501
C	-0.36738	-0.9979	0.890884
C	-1.39851	-0.39688	0.124828
C	-0.95725	0.604508	-0.82173
C	-2.74941	-0.82358	0.306322
C	2.749439	0.823514	-0.3065
C	-3.95952	-0.14143	0.131969
C	-5.1925	-0.93847	0.064608
C	-4.04957	1.325885	0.135316
C	3.959541	0.141408	-0.13208
C	5.192494	0.938501	-0.06465
C	4.049616	-1.32592	-0.13528
C	6.421613	0.462416	-0.58049
C	7.566269	1.250935	-0.55812
C	7.529538	2.541797	-0.02019
C	6.327641	3.03144	0.498132
C	5.180091	2.245614	0.478495
C	3.22361	-2.10487	-0.97867
C	3.301817	-3.49372	-0.98021

C	4.204118	-4.1534	-0.14074
C	5.038102	-3.39993	0.693262
C	4.968643	-2.01141	0.692179
C	-4.9689	2.011443	-0.69175
C	-5.03836	3.399956	-0.69268
C	-4.20408	4.153359	0.141088
C	-3.30149	3.493603	0.980187
C	-3.22329	2.104761	0.978506
C	-6.42159	-0.46225	0.580384
C	-7.5663	-1.25068	0.558055
C	-7.52966	-2.54159	0.020231
C	-6.32779	-3.03136	-0.49805
C	-5.18018	-2.24562	-0.47846
O	-1.87857	1.059727	-1.70407
O	1.878621	-1.05987	1.703802
H	0.654609	1.730212	-1.64271
H	-0.65458	-1.73032	1.642479
H	-2.83575	-1.83728	0.696772
H	2.835763	1.837229	-0.69692
H	6.461111	-0.52613	-1.02492
H	8.492005	0.861883	-0.97316
H	8.425443	3.155399	-0.00356
H	6.288511	4.026936	0.9321
H	4.262422	2.6229	0.918594
H	2.537595	-1.60352	-1.65307
H	2.663519	-4.06555	-1.64853
H	4.263414	-5.23785	-0.14144
H	5.742095	-3.90069	1.352511
H	5.607399	-1.43925	1.357082
H	-5.6079	1.439337	-1.35646
H	-5.7426	3.90077	-1.35163
H	-4.26338	5.237811	0.141903
H	-2.66296	4.065377	1.648345
H	-2.53705	1.603344	1.652631
H	-6.46102	0.526348	1.024714
H	-8.49202	-0.86153	0.973046
H	-8.42561	-3.15512	0.00363
H	-6.28873	-4.02689	-0.93195
H	-4.26254	-2.623	-0.91852
H	-1.48998	1.766039	-2.23855
H	1.490016	-1.76616	2.238302

Table S12. Calculated coordinate of CEOCH in the ground state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program.

Atom	x	y	z
O	0.779884	-2.38349	1.170245
C	0.357168	-1.21412	0.593489
C	1.373553	-0.38837	0.051671
C	3.925377	-0.17044	0.045867
C	5.212599	-0.90464	-0.09249
C	2.757692	-0.86646	0.067524
H	2.839917	-1.94857	0.106366

C	-0.97725	-0.8211	0.545954
H	-1.73936	-1.4431	0.992755
C	4.010441	1.311808	0.209705
C	6.37421	-0.45706	0.564398
H	6.329278	0.44393	1.167444
C	4.685016	2.102598	-0.73594
H	5.141046	1.624728	-1.59804
C	7.572093	-1.16176	0.466623
H	8.451229	-0.80067	0.992946
C	3.447489	1.946394	1.329272
H	2.936288	1.344889	2.074098
C	5.307885	-2.07238	-0.8726
H	4.438051	-2.41353	-1.425
C	7.644546	-2.32679	-0.29914
H	8.580015	-2.87263	-0.38
C	-0.19923	-3.29378	1.646394
H	-0.76472	-2.87549	2.488889
H	0.350248	-4.17244	1.988183
H	-0.90203	-3.58591	0.856405
C	4.767619	3.486561	-0.58291
H	5.285208	4.081063	-1.33053
C	3.537999	3.328753	1.487829
H	3.100701	3.799554	2.363775
C	4.193577	4.105376	0.529503
H	4.26469	5.18211	0.653532
C	6.506028	-2.77679	-0.97006
H	6.553807	-3.672	-1.58381
O	-0.77988	2.383496	-1.17024
C	-0.35717	1.214124	-0.59348
C	-1.37355	0.388376	-0.05166
C	-3.92538	0.17044	-0.04587
C	-5.2126	0.904639	0.092493
C	-2.75769	0.866458	-0.06752
H	-2.83992	1.948574	-0.10636
C	0.977248	0.821106	-0.54595
H	1.73936	1.443099	-0.99275
C	-4.01044	-1.31181	-0.20971
C	-6.37421	0.457056	-0.5644
H	-6.32928	-0.44393	-1.16745
C	-4.68502	-2.1026	0.735935
H	-5.14105	-1.62474	1.598029
C	-7.57209	1.161762	-0.46663
H	-8.45123	0.800674	-0.99296
C	-3.44748	-1.94639	-1.32928
H	-2.93628	-1.34488	-2.0741
C	-5.30789	2.07238	0.872607
H	-4.43806	2.413524	1.425011
C	-7.64455	2.32679	0.299138
H	-8.58002	2.872622	0.38
C	0.199228	3.29378	-1.64639
H	0.764722	2.875484	-2.48888
H	-0.35025	4.172438	-1.98818
H	0.902036	3.58591	-0.8564

C	-4.76762	-3.48656	0.582893
H	-5.28521	-4.08107	1.330509
C	-3.53799	-3.32875	-1.48784
H	-3.10069	-3.79955	-2.36379
C	-4.19357	-4.10537	-0.52952
H	-4.26468	-5.18211	-0.65355
C	-6.50604	2.776779	0.970063
H	-6.55382	3.671987	1.583817

Table S13. Calculated coordinate of CEOCH in the excited state based on B3LYP/6-31G(d,p) level, Gaussian 09 Program.

Atom	x	y	z
O	0.707266	-2.37906	1.205365
C	0.311703	-1.2202	0.610683
C	1.39109	-0.37161	0.155144
C	3.945934	-0.13551	0.147535
C	5.169454	-0.92414	-0.05603
C	2.734135	-0.82512	0.293468
H	2.820348	-1.8819	0.52302
C	-1.01009	-0.85333	0.467905
H	-1.79059	-1.48633	0.859866
C	4.059366	1.327264	0.27081
C	6.428366	-0.48071	0.416904
H	6.492929	0.468282	0.938035
C	4.899987	2.076946	-0.58511
H	5.463887	1.559498	-1.35474
C	7.572708	-1.25376	0.258055
H	8.521327	-0.89089	0.644125
C	3.332315	2.03638	1.256146
H	2.701689	1.481234	1.942316
C	5.12847	-2.1838	-0.70223
H	4.187455	-2.53608	-1.11222
C	7.506758	-2.49722	-0.379
H	8.40193	-3.0997	-0.50205
C	-0.28685	-3.2863	1.665628
H	-0.88893	-2.84333	2.467993
H	0.255437	-4.14905	2.054502
H	-0.95033	-3.60128	0.851946
C	4.990671	3.460913	-0.47551
H	5.632373	4.011968	-1.15751
C	3.433899	3.419129	1.369843
H	2.875842	3.935186	2.146528
C	4.257823	4.14342	0.501896
H	4.33418	5.223152	0.590702
C	6.275581	-2.95427	-0.85763
H	6.212493	-3.91196	-1.36724
O	-0.70723	2.379025	-1.20526
C	-0.31167	1.22015	-0.61059
C	-1.39106	0.371566	-0.15506
C	-3.94591	0.135494	-0.14751
C	-5.16941	0.924141	0.056137
C	-2.7341	0.825091	-0.29338
H	-2.82029	1.881884	-0.52285
C	1.010123	0.853287	-0.46782

H	1.790631	1.486284	-0.85977
C	-4.0594	-1.32726	-0.27093
C	-6.42833	0.4808	-0.41685
H	-6.49293	-0.46814	-0.93807
C	-4.90001	-2.07701	0.58495
H	-5.46384	-1.55962	1.354671
C	-7.57265	1.25387	-0.25792
H	-8.52128	0.891063	-0.64403
C	-3.33245	-2.0363	-1.2564
H	-2.70185	-1.4811	-1.94255
C	-5.12839	2.183736	0.702456
H	-4.18736	2.535955	1.112473
C	-7.50666	2.497263	0.37925
H	-8.40182	3.099758	0.502362
C	0.286886	3.28627	-1.66551
H	0.888973	2.843301	-2.46788
H	-0.2554	4.14902	-2.05438
H	0.950364	3.601239	-0.85182
C	-4.99076	-3.46096	0.475198
H	-5.63244	-4.01206	1.15717
C	-3.4341	-3.41903	-1.37025
H	-2.87612	-3.93502	-2.14703
C	-4.258	-4.14339	-0.50233
H	-4.33441	-5.2231	-0.59126
C	-6.27547	2.954226	0.857925
H	-6.21236	3.911868	1.367623

^{1}H and ^{13}C NMR spectra of CEH, CECH, CEOH and CEOCH

Figure S15. ^{1}H (left) and ^{13}C (right) NMR spectra of CEH.

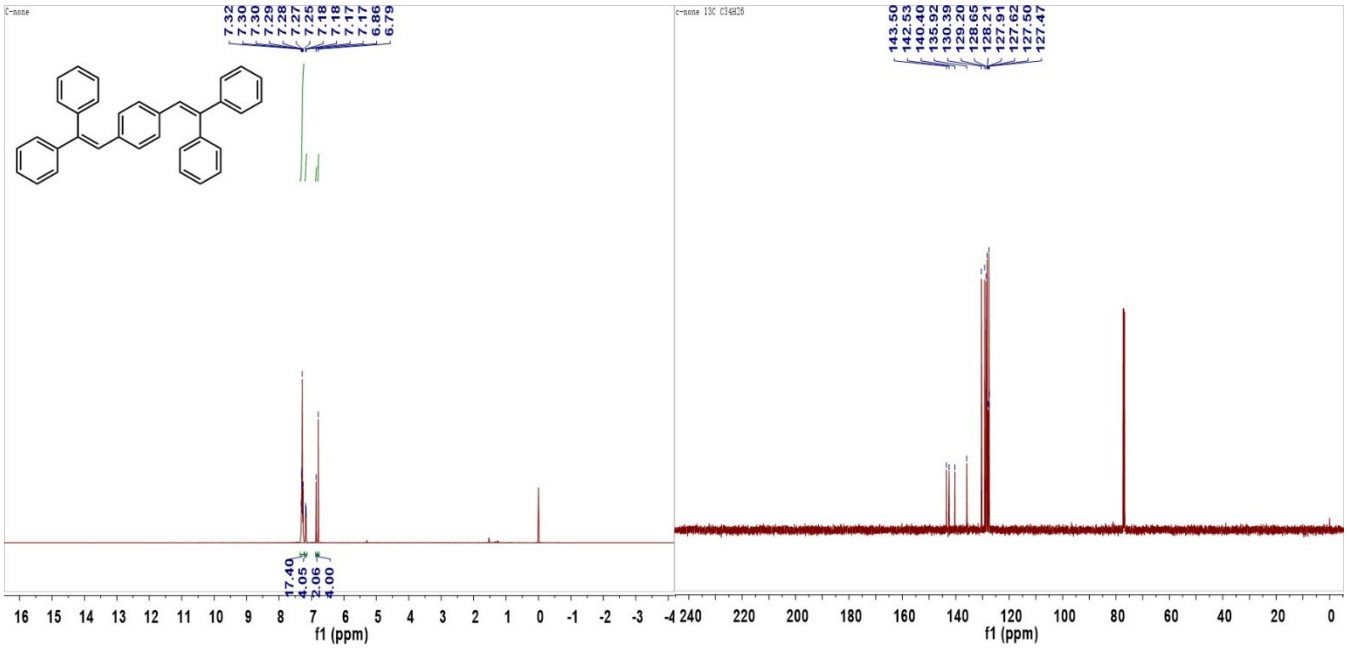


Figure S16. ^{1}H (left) and ^{13}C (right) NMR spectra of CECH.

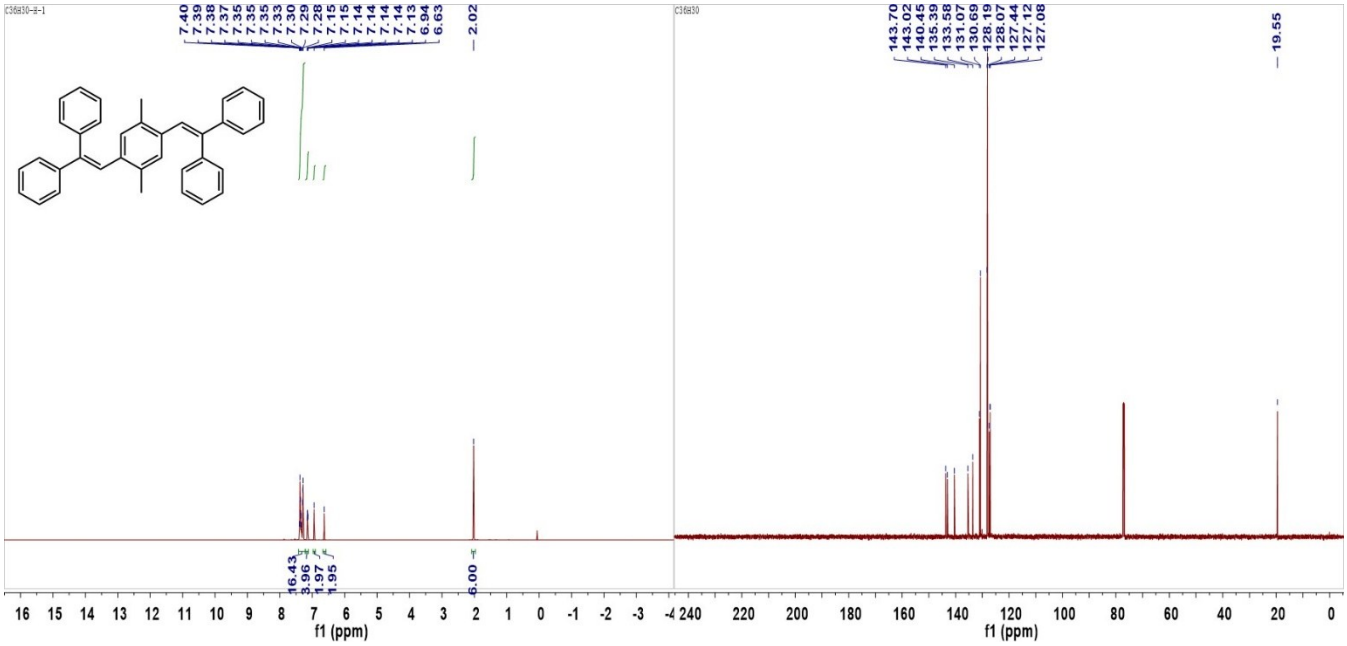


Figure S17. ^{1}H (left) and ^{13}C (right) NMR spectra of CEOH.

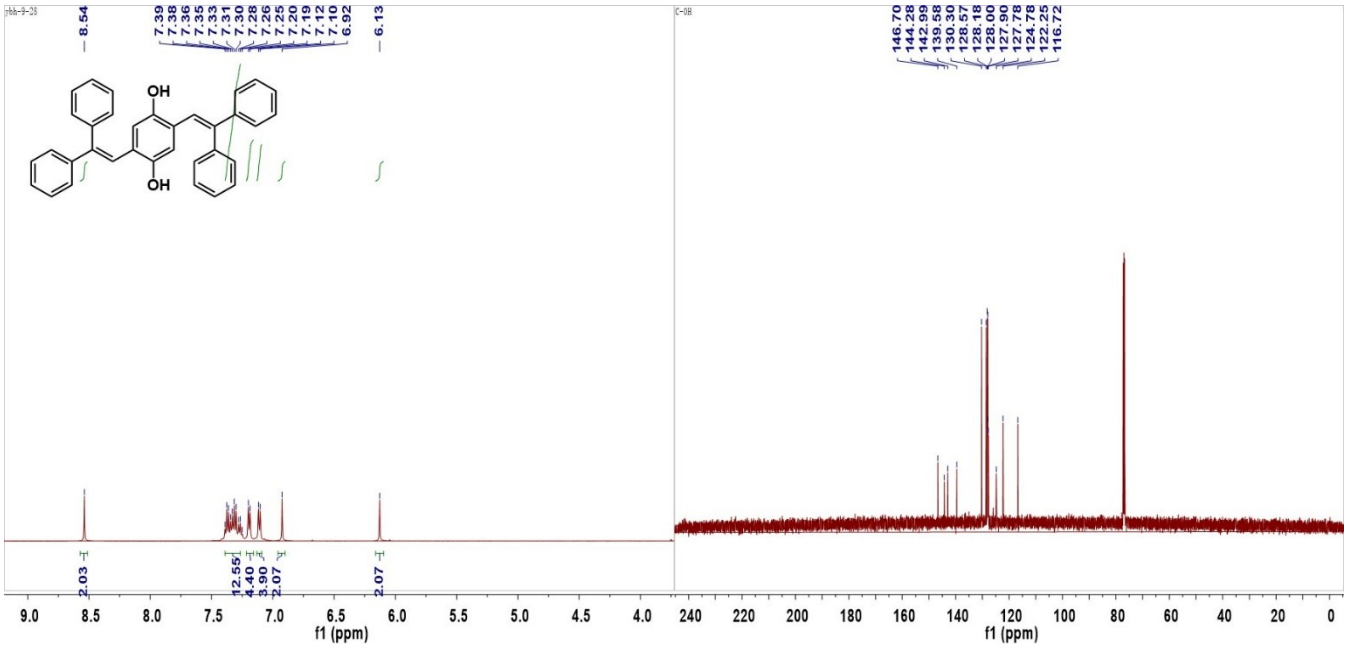
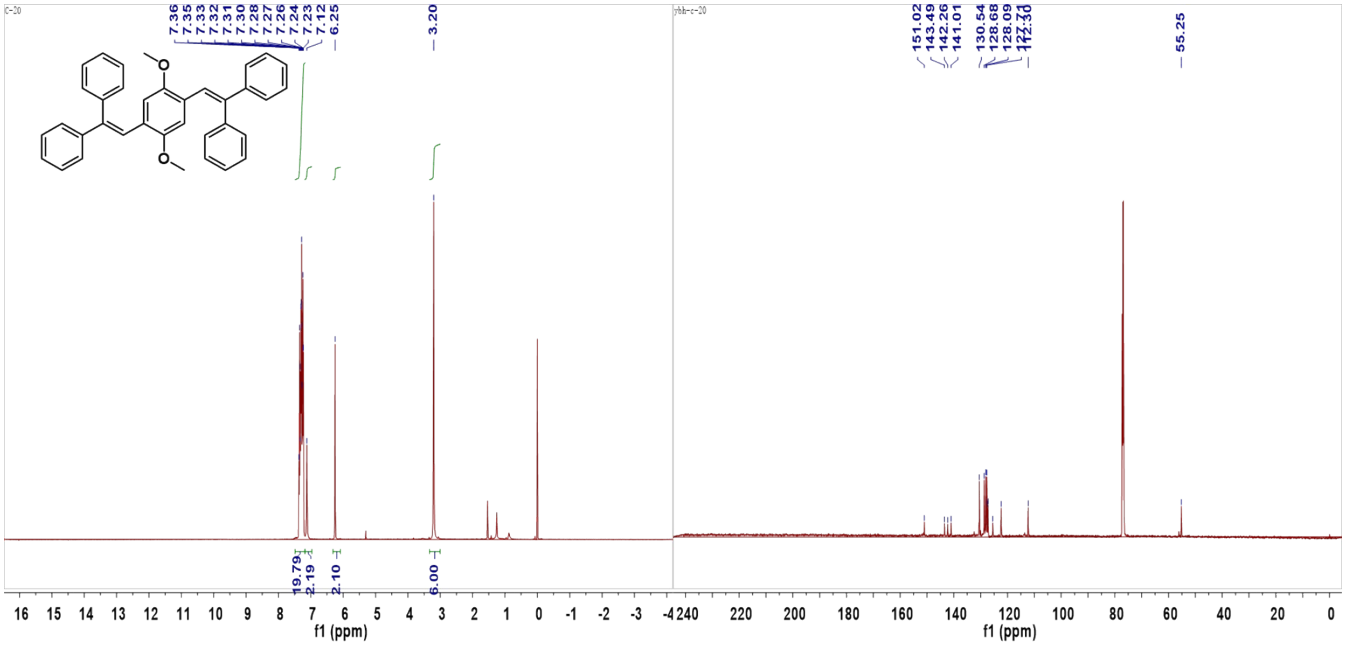


Figure S18. ^{1}H (left), ^{13}C (right) NMR and NOESY NMR spectra (bottom) of CEOCH.



References

1 Park, Y. I.; Kuo, C. Y.; Martinez, J. S.; Park, Y. S.; Postupna, O.; Zhugayevych, A.; Kim, S.; Park, J.; Tretiak, S.; Wang, H. L., Tailored electronic structure and optical properties of conjugated systems through aggregates and dipole-dipole interactions. ACS Appl Mater Interfaces 2013, 5 (11), 4685-95.

2 Kokado, K.; Taniguchi, R.; Sada, K., Rigidity-induced emission enhancement of network polymers crosslinked by tetraphenylethene derivatives. Journal of Materials Chemistry C 2015, 3 (33), 8504-8509.

3 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.