Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Utilizing aggregation-induced emission phenomenon to visualize spontaneous molecular directed motion in solid state

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Contents:

1. Materials

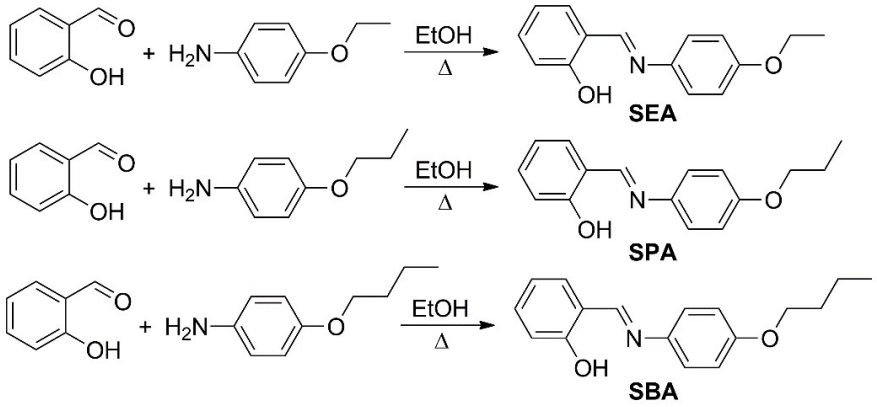
Unless otherwise noted, all chemical reagents and solvents were commercially available and were used without further purification. Salicylaldehyde and *p*-phenetidine were purchased from Energy Chemical Co., Shanghai, China. *p*-propoxyaniline were purchased from Alfa Aesar (China) Chemical Co., Ltd. *p*-butoxyaniline were purchased from Tokyo Chemical Industry Co., Ltd. All the other reagents and solvents were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China. Deionized water was used throughout all experiments.

2. Characterization

Absorption spectra were recorded by using a JASCO-750 UV-vis spectrometer. Fluorescence spectra were obtained by using a JASCO FP-8300 spectrometer. The temperatures in fluorescence measurements were controlled by an ETC-815 peltier thermostatted single cell holder, which offered a temperature control accuracy of ±0.1°C. Dynamic light scattering (DLS) experiments were measured on a NanoPlus-3 DLS particle size/zeta potential analyzer. Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 ADVANCE. The crystallographic data were collected on a Rigaku Saturn 724 CCD diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073Å). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV400 NMR spectrometer operated at 400 MHz and 101 MHz in $CDCl_3$, respectively. Atomic force microscopy (AFM) patterns were obtained by Oxford Instruments MFP-3D Infinity atomic force microscope. Melting point were tested on a XT4A melting point meter (Temperature control type). Electrospray Ionization Mass Spectrometry (ESI-MS) were undertaken using an Agilent Technologies 6420 triple quadrupole LC/MS without using the liquid chromatography part. The photos and videos were taken by a Nikon D5500 camera. Unless otherwise noted, all the measurement experiments were performed at 25 °C.

3. Synthesis

General synthetic procedures of **SEA**, **SPA** and **SBA** are as follows. 10 mmol salicylaldehyde was dissolved in 20 mL absolute ethanol. Then 10 mmol corresponding aniline derivative was added. The mixture was stirred and heated to 80 °C for 30 min. After cooling to room temperature, light yellow precipitate was formed. The resulting precipitate was filtrated and washed with 10 mL of cold absolute ethanol for three times. After being dried under reduced pressure, final product was obtained. The crystal of **SEA**, **SPA** and **SBA** are obtained in *n*-hexane by slowly volatilized at room temperature.



Scheme S1. Synthetic route for **SEA**, **SPA** and **SBA**.

Salicylaldehyde 4-ethyoxyaniline Schiff base (SEA): Schistose yellow crystalline, yield is 75%. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.43 (t, 3H, J = 7.0 Hz), 4.06 (q, 2H, J = 7.0 Hz), 6.93 (t, 3H, J = 7.6 Hz), 7.02 (d, 1H, J = 8.2 Hz), 7.27 (d, 2H, J = 8.9 Hz), 7.36 (dd, 2H, J = 10.7, 7.9 Hz), 8.61 (s, 1H), 13.44 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.85, 63.78, 115.17, 117.17, 118.99, 119.43, 122.30, 131.95, 132.66, 141.22, 158.25, 160.33, 161.01. ESI-MS spectrometry: m/z calcd for $[M + H]^+$: 242.11; found: 242.10. Melting point: 97 °C.

Salicylaldehyde 4-propoxyaniline Schiff base (SPA): Schistose yellow crystalline, yield is 70%. ^{1}H NMR ($CDCl_3$) δ(ppm): 1.05 (t, 3H, J = 7.4 Hz), 1.78-1.88 (m, 2H), 3.95 (t, 2H, J = 6.6 Hz), 6.93 (t, 3H, J = 8.7 Hz), 7.03 (d, 1H, J = 8.2 Hz), 7.27 (d, 2H, J = 9.0 Hz), 7.36 (dd, 2H, J =11.9, 7.5 Hz), 8.61 (s, 1H), 13.45 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 10.54, 22.60, 69.85, 115.20, 117.17, 118.99, 119.42, 122.28, 131.94, 132.65, 141.15, 158.47, 160.28, 161.01. ESI-MS spectrometry: m/z calcd for $[M + H]^+$: 256.13; found: 256.10. Melting point: 78 °C.

Salicylaldehyde 4-butoxyaniline Schiff base (SBA): Schistose crystalline, yield is 72%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.99 (t, 3H, J = 7.4 Hz), 1.45-1.556 (m, 3H), 1.74-1.83 (m, 2H), 3.99 (t,

2H, J = 1.0 Hz), 6.93 (t, 3H, J = 8.2 Hz), 7.02 (d, 1H, J = 8.0 Hz), 7.27 (d, 2H, J = 9.0 Hz), 7.36 (dd, 2H, J = 12.0, 7.5 Hz), 8.61 (s, 1H), 13.46 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.86, 19.24, 31.30, 68.03, 115.19, 117.18, 119.00, 119.32, 122.25, 131.97, 132.75, 140.93, 158.50, 160.23, 161.03. ESI-MS spectrometry: m/z calcd for $[M + H]^+$: 270.14; found: 270.10. Melting point: 74 ^{o}C.

4. Test method of the fluorescence in solid state

A special sample cell was used (Figure S1), which was composed of a quartz glass cuvette and a glass sheet. As shown in Figure S1, the samples are covered on the glass sheet and ground. Then the glass sheet with the ground samples are quickly transferred to a quartz glass cuvette, which was placed in a temperature control device of the fluorescence spectrophotometer to adjust the temperature to the desired temperature. Then the spectra were recorded.

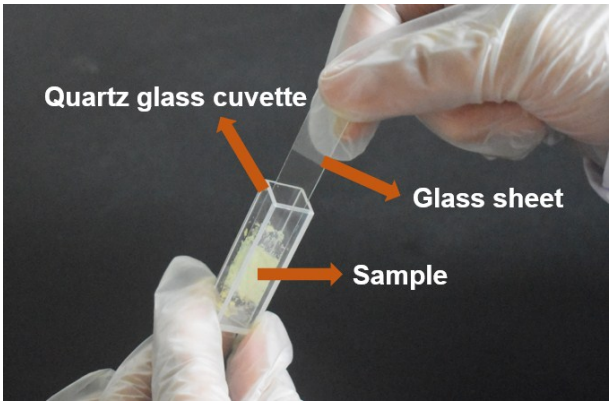


Figure S1. A photo of the special sample cell for fluorescence measurements.

5. Computational Methods

The DFT calculations were performed using the Gaussian 09 program.[1] The geometries were fully optimized using m062x method.[2, 3] Basis set 6-31+G(d，p) was employed for all atoms. Frequency calculations at the same level of theory were carried out to identify all of the stationary points as minima that have zero imaginary frequency.

Reference:

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et. al. Gaussian09, Revision C.01, **2010**.

[2] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, *120*, 215-241.

[3] Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, **200**8, *41*, 157-167.

6. Caption of video

Video 1. SBA was ground and kept in 25 °C. The video was taken under the irradiation of 365 nm UV light.

7. Selected spectra and data referred in the paper

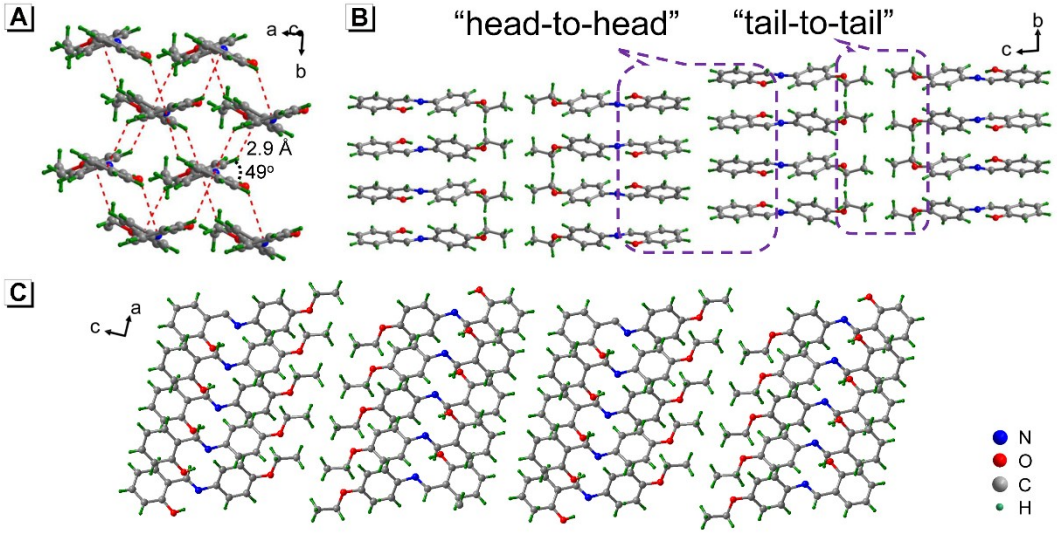


Figure S2. Crystal structure of **SEA** viewed from different directions.

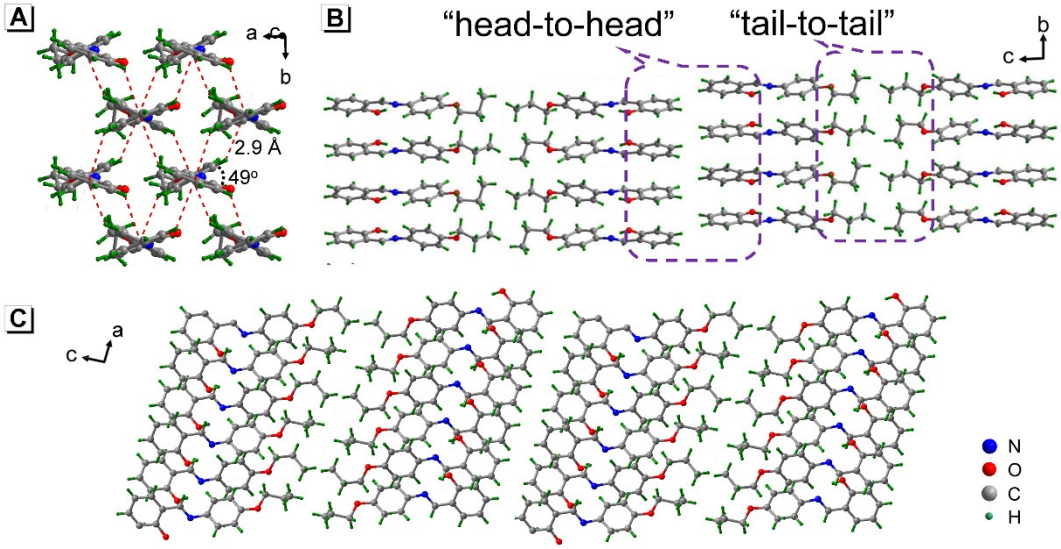
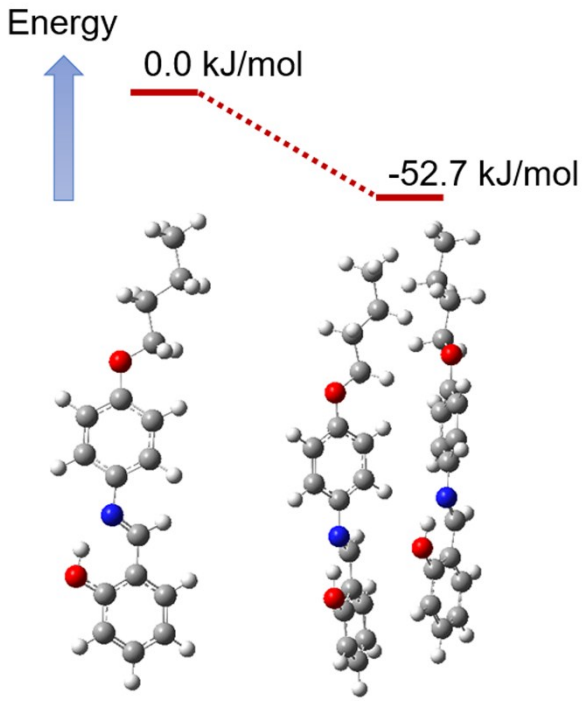


Figure S3. Crystal structure of **SPA** viewed from different directions.



105

106 **Figure S4.** The calculate binding energy of **SBA**.

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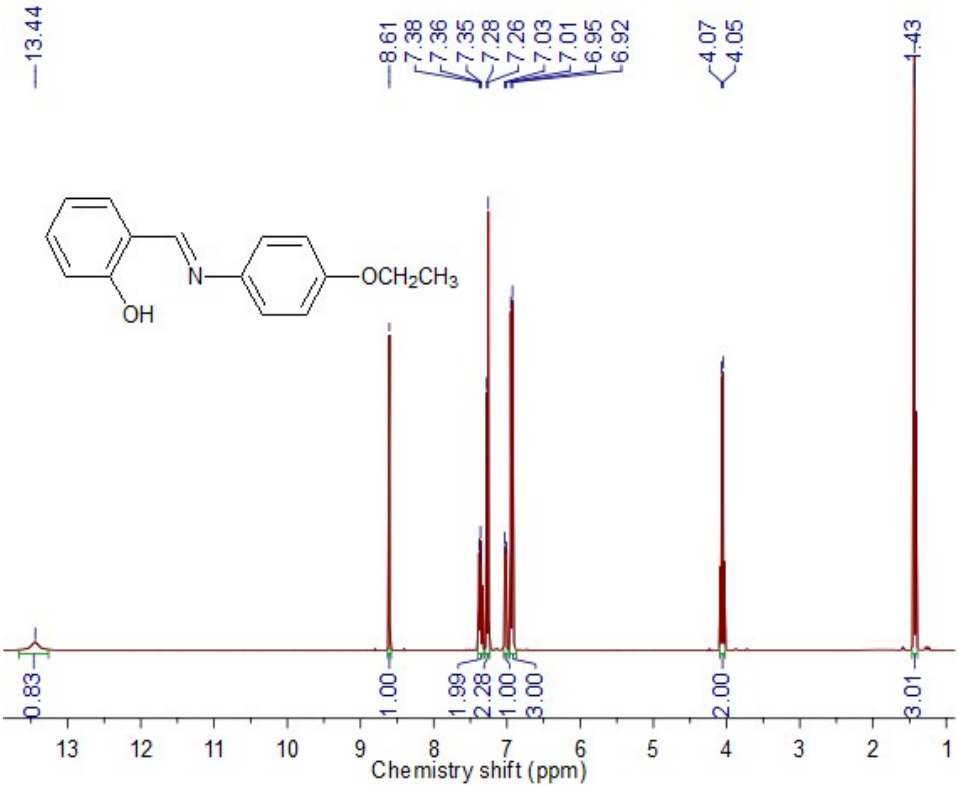
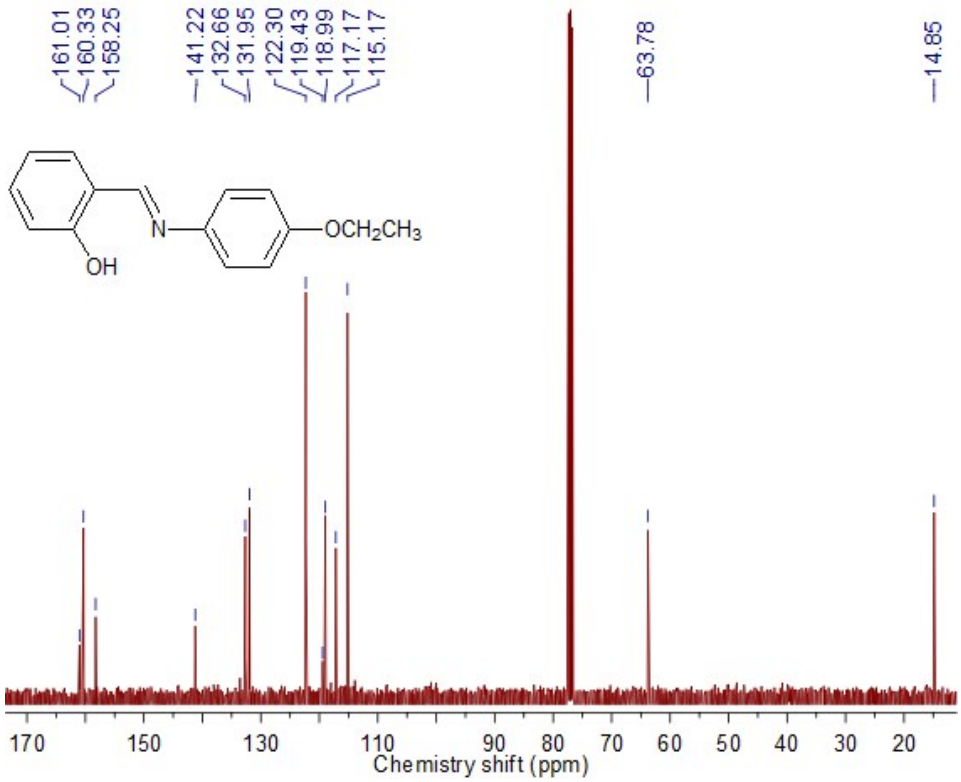


108

109 **Figure S5.** The ^{1}H NMR spectrum of **SEA**.

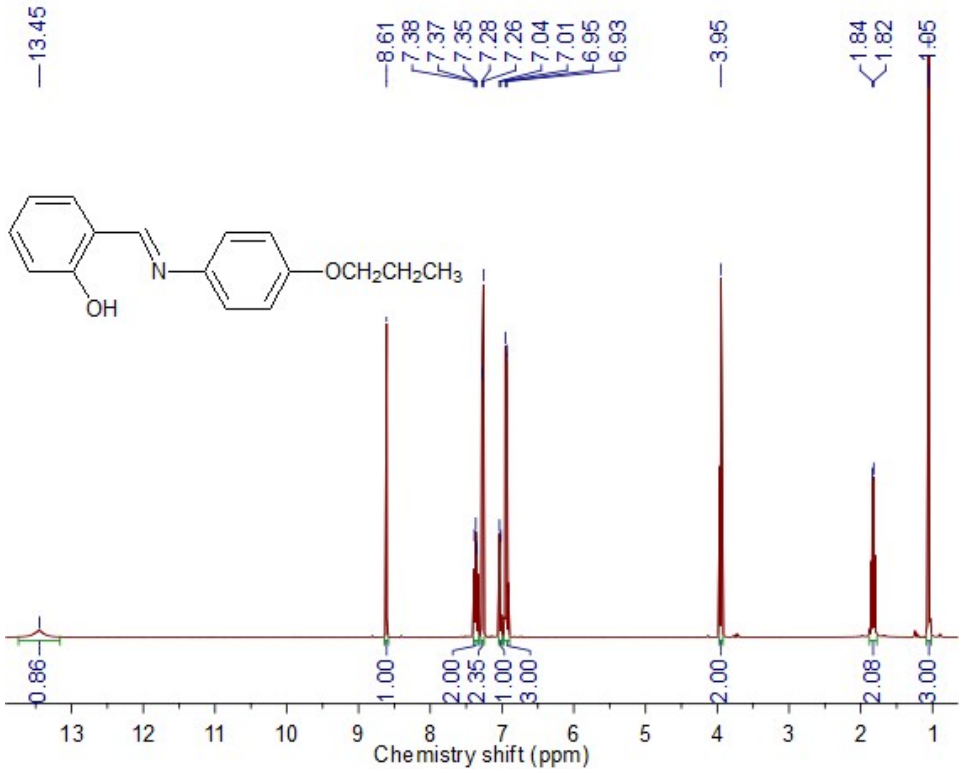
110



111

112 **Figure S6.** The ^{13}C NMR spectrum of **SEA**.

113



114

115 **Figure S7.** The ^{1}H NMR spectrum of **SPA**.

116

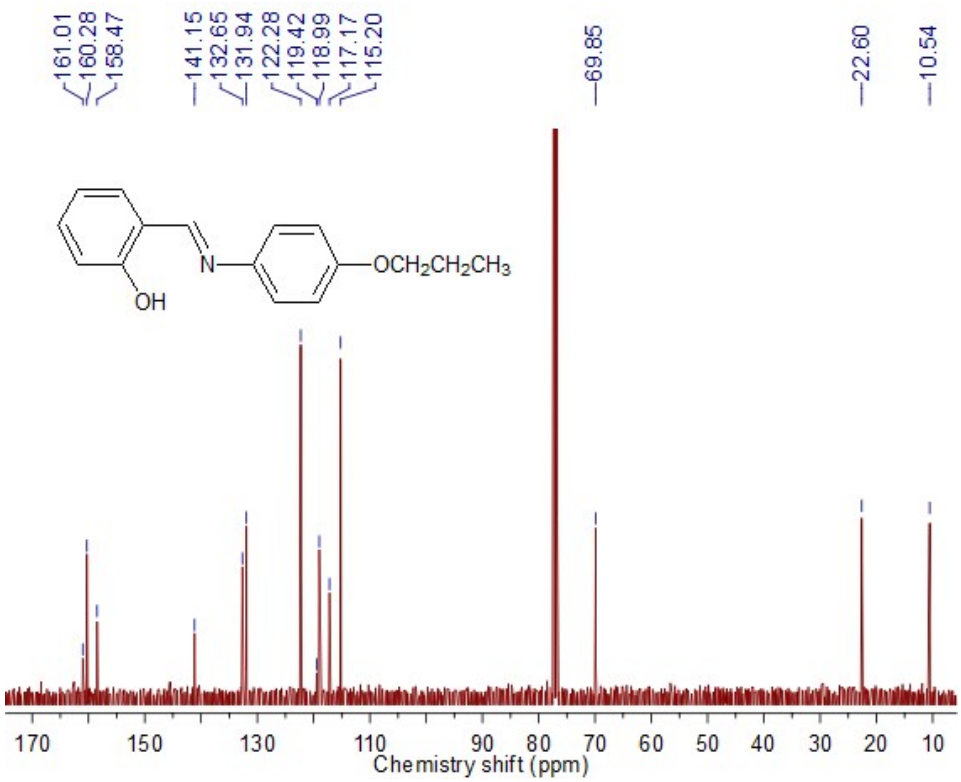


Figure S8. The ^{13}C NMR spectrum of **SPA**.

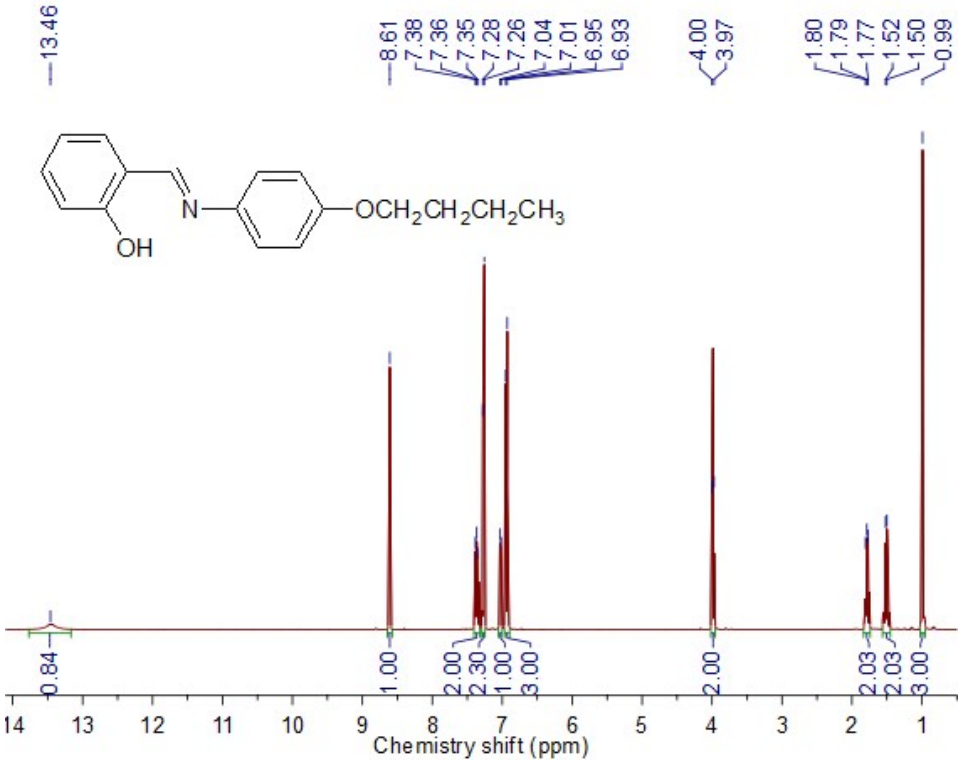
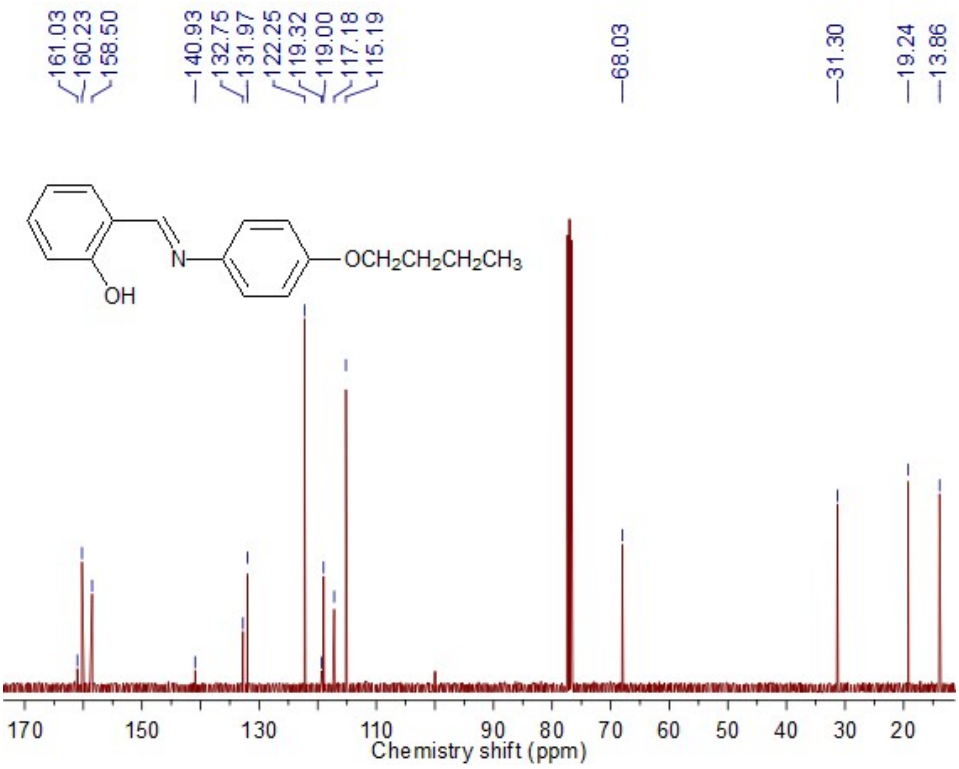


Figure S9. The ^{1}H NMR spectrum of **SBA**.



123

124 **Figure S10.** The ^{13}C NMR spectrum of **SBA**.

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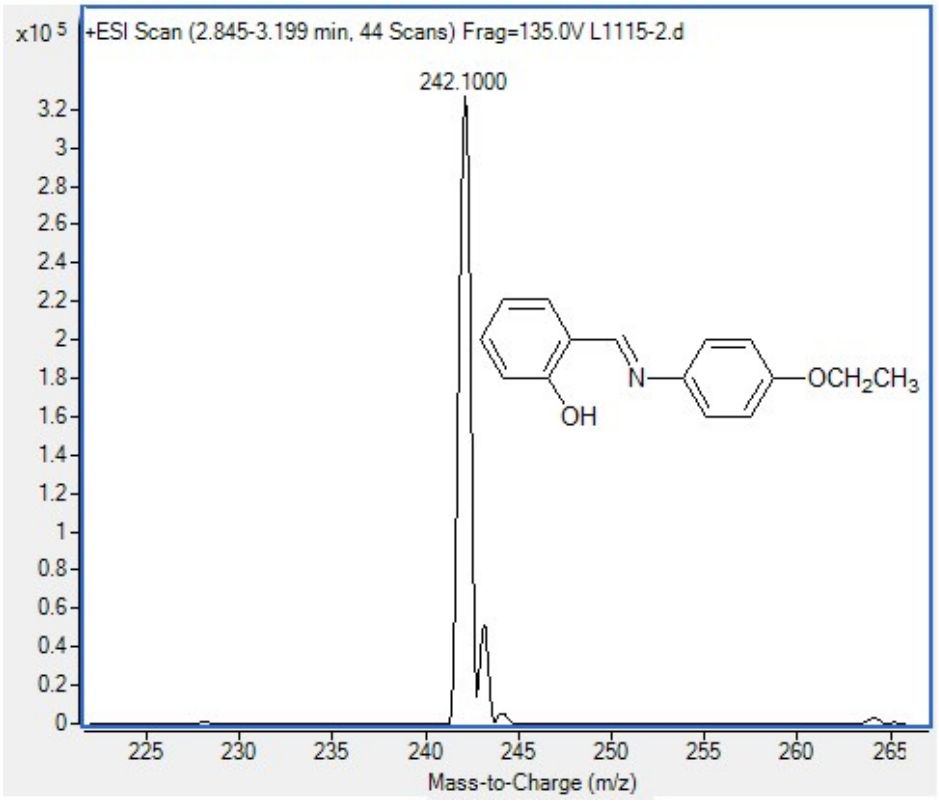

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127 **Figure S11.** The mass spectrometry of **SEA**.

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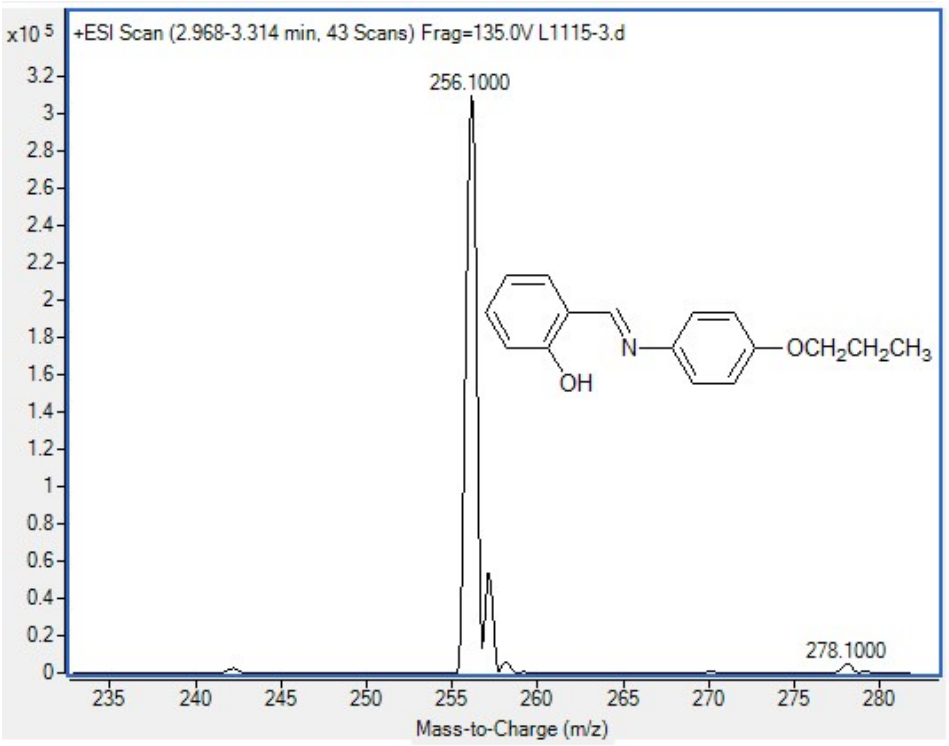
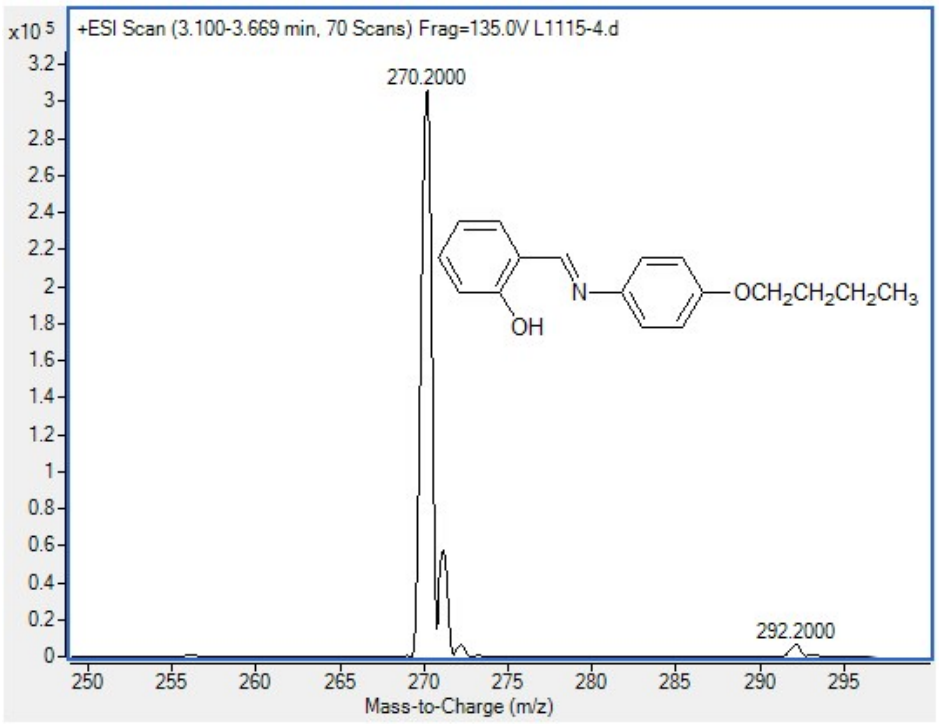


129

130 **Figure S12.** The mass spectrometry of **SPA**.

131



132

133 **Figure S13.** The mass spectrometry of **SBA**.

134

Table S1. The calculated k and $t_{1/2}$ from 15 °C to 20 °C.

Temperature(°C)	15	16	17	18	19	20
k (10^{-4} s^{-1})	5.12	7.07	8.64	13.33	15.82	23.75
$t_{1/2}$ (s)	1353	979	802	520	438	292

Table S2. Crystallographic data and structure refinement details for **SEA**.

Complex	**SEA**
Formula	$C_{15}H_{15}NO_2$
CCDC	1941969
F_w	241.28
Temp.(K)	273.15
Wavelength(Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
a(Å)	6.2682(5)
b(Å)	7.1504(5)
c(Å)	28.857(2)
α(°)	94.165(2)
β(°)	90.331(3)
γ(°)	90.002(3)
V(Å^3)	1289.92(17)
Z	4
Dc(g·cm^{-3})	1.242
μ(mm^{-1})	0.083
F(000)	512.0
GOF on F^2	1.040
R_1[a] (I>2σ(I))	0.0591
wR_2[b] (I>2σ(I))	0.1616

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S3. Crystallographic data and structure refinement details for **SPA**.

Complex	**SPA**
Formula	$C_{16}H_{17}NO_2$
CCDC	1941970
F_w	255.30
Temp.(K)	293(2)
Wavelength(Å)	1.54184
Crystal system	Triclinic
Space group	*P*-1
a(Å)	6.2328(2)
b(Å)	7.21290(10)
c(Å)	31.0245(7)
α(°)	92.777(2)
β(°)	94.558(2)
γ(°)	90.014(2)
V(Å^3)	1388.70(6)
Z	4
Dc(g·cm^{-3})	1.221
μ(mm^{-1})	0.642
F(000)	544
GOF on F^2	1.000
R_1[a][I>2σ(I)]	0.0468
wR_2[b][I>2σ(I)]	0.1319

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

142 **Table S4.** Crystallographic data and structure refinement details for **SBA**.

Complex	**SBA**
Formula	$C_{17}H_{19}NO_2$
CCDC	1941971
F_w	269.33
Temp.(K)	100 K
Wavelength(Å)	1.54184
Crystal system	Triclinic
Space group	*P*-1
a(Å)	6.1745(2)
b(Å)	7.0411(2)
c(Å)	33.2296(10)
α(°)	86.545(2)
β(°)	84.929(2)
γ(°)	89.992(2)
V(Å^3)	1436.38(8)
Z	4
Dc(g·cm^{-3})	1.245
μ(mm^{-1})	0.647
F(000)	576.0
GOF on F^2	1.119
R_1[a] (I>2σ(I))	0.0490
wR_2[b] (I>2σ(I))	0.1306

143 [a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

144

145 **Table S5.** Geometrical coordinates of the compound showed in Figure S4 left.

O	3.71346	0.74608	-0.2713
O	-4.12224	1.76363	0.56807
H	-3.14468	1.64682	0.45548
N	-1.83913	0.56832	0.04311
C	2.36707	0.61441	-0.15806
C	-3.96239	-0.53897	-0.11989
C	1.61019	1.72769	-0.54568
H	2.13557	2.60681	-0.90231
C	-0.43027	0.54491	-0.01263
C	-4.70587	0.59986	0.27061
C	0.23139	1.69598	-0.46082
H	-0.36145	2.55642	-0.75357
C	1.72131	-0.52505	0.32302
H	2.28466	-1.38751	0.65734
C	-4.6404	-1.72917	-0.4227
H	-4.0559	-2.59583	-0.72248
C	0.32975	-0.55155	0.39337
H	-0.16426	-1.42675	0.80458
C	-6.10149	0.51133	0.34912
H	-6.65125	1.39603	0.65034
C	4.5237	-0.34618	0.12472
H	4.26497	-1.23919	-0.46348
H	4.34703	-0.57964	1.18526
C	-2.51164	-0.4944	-0.21313
H	-2.01037	-1.41962	-0.52847
C	5.97196	0.03991	-0.10169
H	6.18902	0.94629	0.47519
H	6.10677	0.29558	-1.15901
C	-6.01861	-1.81115	-0.34342
H	-6.53062	-2.73699	-0.57881
C	-6.74279	-0.6781	0.04607
H	-7.82535	-0.72821	0.11266
C	6.93166	-1.07952	0.29566
H	6.77532	-1.33616	1.35088
H	6.69596	-1.98326	-0.28009
C	8.3915	-0.69544	0.07228
H	8.65539	0.18994	0.65841
H	8.57644	-0.46371	-0.98093
H	9.06652	-1.50431	0.36217

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147 **Table S6.** Geometrical coordinates of the compound showed in Figure S4 right.

O	-2.63471	-3.16768	0.23242	O	-4.68050	1.54203	0.55709
O	5.27336	-2.51128	0.54823	O	2.99569	0.38409	1.88329
H	4.28847	-2.61561	0.49091	H	2.03532	0.59150	1.76931
N	2.80870	-2.12462	-0.28068	N	0.85980	1.67135	1.04581
C	-1.32476	-2.83294	0.09295	C	-0.53502	1.71354	0.86144
C	4.68476	-0.89576	-1.13617	C	3.08840	2.36705	0.51165
C	-0.40082	-3.87908	0.20871	C	-2.52366	1.92672	-0.51669
H	-0.77556	-4.87856	0.40054	H	-2.95934	2.11160	-1.49091
C	1.41854	-2.33096	-0.17123	C	-1.13664	1.98073	-0.36820
C	5.63026	-1.56808	-0.32672	H	-0.51887	2.18551	-1.23806
C	0.95439	-3.62659	0.09181	C	-3.32434	1.61271	0.58309
H	1.67809	-4.42922	0.19049	C	3.70000	1.32988	1.25600
C	-0.87345	-1.53331	-0.13676	C	1.64295	2.47262	0.41693
H	-1.56357	-0.69973	-0.19459	H	1.24347	3.27686	-0.2171
C	5.12233	0.10656	-2.01200	C	-2.72397	1.32933	1.81797
H	4.38091	0.63056	-2.61083	H	-3.36514	1.07183	2.65423
C	0.49127	-1.29412	-0.26916	C	-1.34900	1.36359	1.94836
H	0.83798	-0.27559	-0.40533	H	-0.87514	1.12161	2.89391
C	6.98500	-1.22992	-0.43305	C	-5.33863	1.77491	-0.67719
H	7.69280	-1.76155	0.19345	H	-5.05829	0.99105	-1.39841
C	-3.58320	-2.11891	0.15233	H	-5.02649	2.74275	-1.09487
H	-3.50284	-1.61088	-0.82197	C	5.09834	1.27421	1.33492
H	-3.38344	-1.36705	0.93051	H	5.54231	0.46127	1.89930
C	3.26551	-1.20272	-1.04695	C	5.27738	3.24648	-0.06527
H	2.59776	-0.60442	-1.68185	H	5.89272	3.97847	-0.57585
C	-4.96724	-2.71066	0.32513	C	3.90051	3.31069	-0.14204
H	-5.02744	-3.19764	1.30537	H	3.41782	4.10288	-0.70997
H	-5.11950	-3.49066	-0.42967	C	-6.83402	1.77027	-0.42421
C	6.46200	0.43888	-2.11243	H	-7.08917	2.62468	0.21314
H	6.78648	1.21948	-2.79126	H	-7.09571	0.86695	0.13774
C	7.38985	-0.24179	-1.31672	C	5.86952	2.21669	0.68072
H	8.44489	0.00655	-1.38688	H	6.95128	2.14580	0.73890
C	-6.04190	-1.63364	0.20416	C	-7.63423	1.81906	-1.72363
H	-5.82759	-0.83035	0.92074	H	-7.34067	2.70145	-2.30613
H	-5.98051	-1.17499	-0.79318	H	-7.37867	0.94468	-2.33582
C	-7.45052	-2.17558	0.42652	C	-9.13894	1.84614	-1.47177
H	-7.55023	-2.60581	1.42744	H	-9.45472	0.96011	-0.91209
H	-7.68531	-2.96101	-0.29837	H	-9.70093	1.86982	-2.40831
H	-8.20425	-1.38910	0.32316	H	-9.42109	2.72648	-0.88670

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