Supplementary Information (SI) for Journal of Materials Chemistry C.

General Information.

The chemicals used in the experiments, including benzoic acid, terephthalic acid, trimesic acid, pyromellitic acid, benzenepentacarboxylic acid, 4-dimethylaminopyridine (DMAP), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI), 3-buten-1-ol, acrylamide, and azobisisobutyronitrile (AIBN), along with all other inorganic salts and organic reagents utilized during the experiments, were purchased from domestic chemical suppliers (Aladdin, Macklin, Titan, Bide Pharm, etc.).

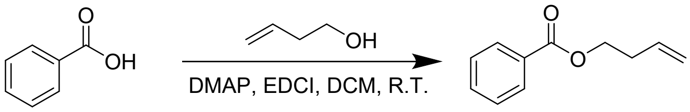
^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-600 spectrometer. The electronic spray ionization (ESI) and direct analysis in real time (DART) high-resolution mass spectra (HRMS) were tested on a Waters LCT Premier XE spectrometer. The UV-Vis absorption spectra were obtained on a Cary 60 (Agilent Technologies) spectrophotometer. The delayed spectra and time-resolved delayed spectra were recorded on an Agilent Cary Eclipse spectrophotometer. Phosphorescence mode; Delay time = 0.1 ms; Gate time = 2.0 ms. Absolute PL quantum yields were determined with a spectrometer C11347-11 (Hamamatsu, Japan). Powder X-ray diffraction (XRD) was performed on a D/max2550V. Aqueous gel permeation chromatography (GPC) was performed on a Series 200. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed with the Gaussian 09 (Revision E.01) software package. The ground-state (S_0) geometries were optimized with the B3LYP and 6- 311G* basis. The excitation energies in the singlet and triplet states were obtained using TD-DFT method based on the optimized S0 molecular structure.

Preparation of Polymers.

Synthesis of carboxylic acid derivatives.

Carboxylic acid derivatives (CADs) E1-E5 were synthesized according to reported methods[1]. The complete synthesis for E1 is as follows, while for E2-E5, only the differing details (such as reagent quantities or specific conditions) will be provided.

But-3-en-1-yl benzoate (E1)

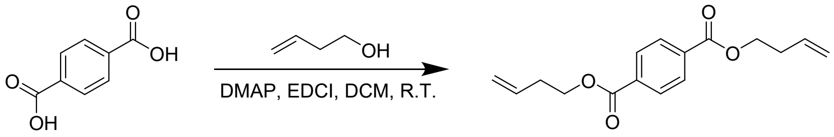


Benzoic acid (1.00 g, 8.19 mmol, 1.0 eq), 3-butene-1-ol (0.83 g, 11.47 mmol, 1.4 eq), EDCI (3.83 g, 19.98 mmol, 2.44 eq), and DMAP (2.44 g, 19.98 mmol, 2.44 eq) were added to a 250 mL round-bottom flask with dichloromethane (DCM, 100 mL) as the solvent. The mixture was stirred at R.T. overnight. Afterward, the reaction mixture was filtered to remove insoluble substances. The crude product was purified by column chromatography (PE/EA = 100:1) to yield compound E1 as colorless oil (672 mg, yield 46.7%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.01 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 5.94-5.82 (m, 1H), 5.24-5.06 (m, 2H), 4.38 (t, *J* = 6.7 Hz, 2H), 2.53 (q, *J* = 6.7 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 166.50, 134.02, 132.84, 130.33, 128.30, 117.31, 63.94, 33.15. HRMS (ESI) (m/z): [M+H]$^+$ calcd for [C$_{11}$H$_{13}$O$_2$]$^+$, 177.0910; found, 177.0909.

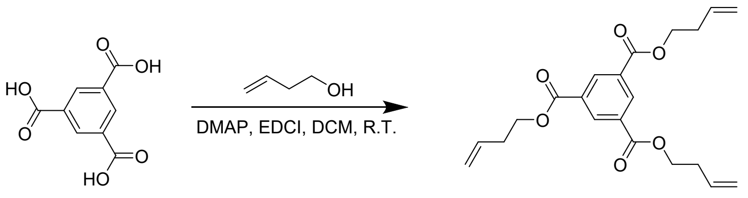
1,4-Benzenedicarboxylic acid, 1,4-di-3-buten-1-yl ester (E2)



Terephthalic acid (1.00 g, 6.02 mmol, 1.00 eq), 3-buten-1-ol (1.13 g, 15.65 mmol, 2.60 eq), EDCI (4.62 g, 24.08 mmol, 4.00 eq), and DMAP (2.44 g, 24.08 mmol, 4.00 eq) were added to a reaction flask. The crude product was purified by column chromatography (PE/EA = 25:1) to yield compound E2 as colorless oil (756 mg, yield 45.8%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (s, 4H), 5.89-5.76 (m, 2H), 5.17-5.02 (m, 4H)., 4.35 (t, *J* = 6.7 Hz, 4H), 2.49 (q, *J* = 6.7 Hz, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.70, 134.07, 133.84, 129.51, 117.51, 64.35, 33.10. HRMS (DART) (m/z): [M+H]$^+$ calcd for [C$_{16}$H$_{19}$O$_4$]$^+$, 275.1278; found, 275.1274.

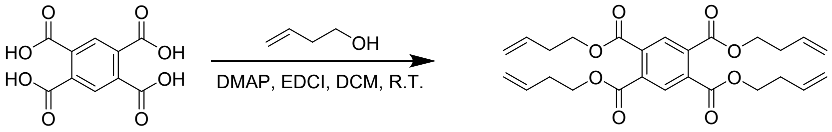
1,3,5-Trimesic acid, 1,3,5-tri-3-buten-1-yl ester (E3)



Trimesic acid (1.00 g, 4.76 mmol, 1.00 eq), 3-buten-1-ol (1.54 g, 21.42 mmol, 4.50 eq), EDCI (7.30 g, 38.08 mmol, 8.00 eq), and DMAP (4.65 g, 38.08 mmol, 8.00 eq) were added to a reaction flask. The crude product was purified by column chromatography (PE/EA = 18:1) to yield compound E3 as a colorless oil (736 mg, yield 41.6%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.79 (s, 3H), 5.91-5.78 (m, 3H), 5.34-5.06 (m, 6H), 4.40 (t, *J* = 6.7 Hz, 6H), 2.53 (q, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.88, 134.49, 133.69, 131.37, 117.61, 64.61, 33.09. HRMS (DART) (m/z): [M+H]$^+$ calcd for [C$_{21}$H$_{25}$O$_6$]$^+$, 373.1646; found, 373.1641.

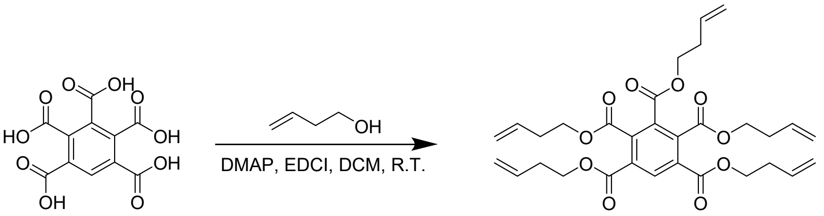
1,2,4,5-Pyromellitic acid, 1,2,4,5-tetra-3-buten-1-yl ester (E4)



Pyromellitic acid (1.00 g, 3.93 mmol, 1.00 eq), 3-buten-1-ol (1.7 g, 23.61 mmol, 6.00 eq), EDCI (8.82 g, 46 mmol, 11.70 eq), and DMAP (5.62 g, 46 mmol, 11.70 eq) were added to a reaction flask. The crude product was purified by column chromatography (PE/EA = 10:1) to yield compound E4 as a pale yellow oil (649 mg, yield 35.1%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 5.89-5.74 (m, 4H), 5.23-5.04 (m, 8H), 4.38 (t, *J* = 6.8 Hz, 8H), 2.50 (q, *J* = 6.7 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.87, 134.35, 133.54, 129.57, 117.69, 65.23, 32.84. HRMS (ESI) (m/z): $[M+H]^+$ calcd for $[C_{26}H_{30}O_8Na]^+$, 493.1833; found, 493.1829.

1,2,3,4,5-Benzenepentacarboxylic acid, 1,2,3,4,5-penta-3-buten-1-yl ester (E5)

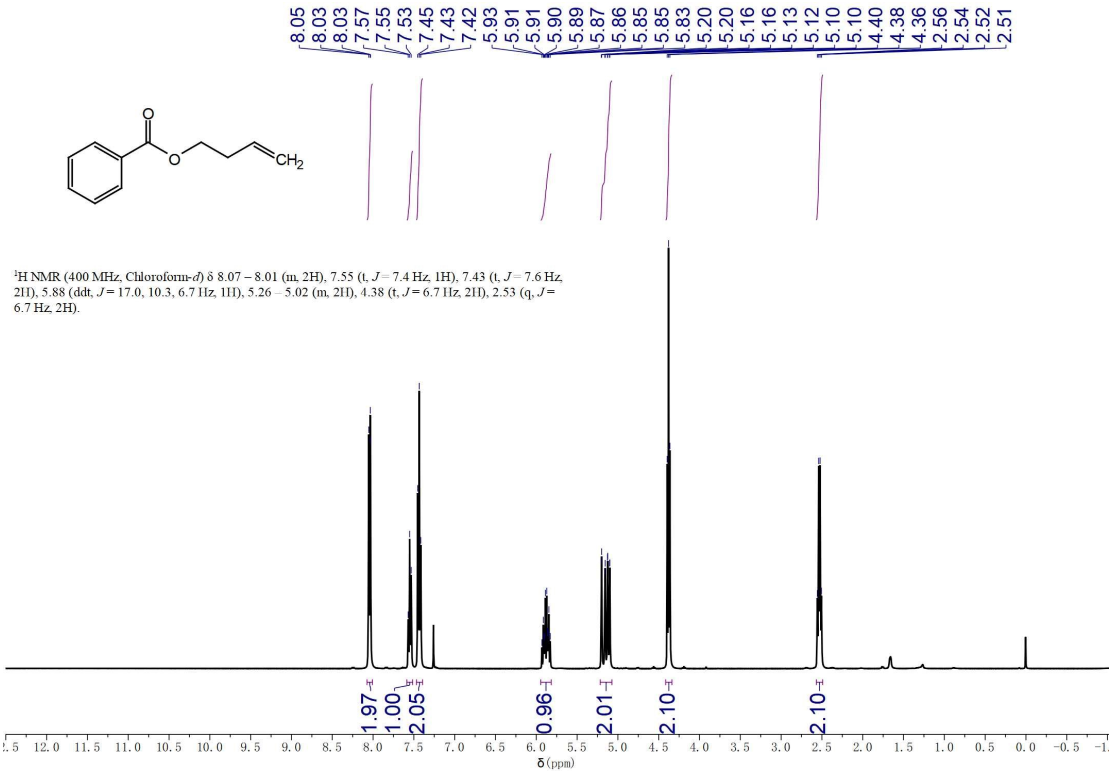


Benzenepentacarboxylic acid (2.00 g, 6.71 mmol, 1.00 eq), 3-buten-1-ol (3.87 g, 53.68 mmol, 8.00 eq), EDCI (15.43 g, 80.52 mmol, 12.00 eq), and DMAP (9.84 g, 80.52 mmol, 12.00 eq) were added to a reaction flask with dichloromethane (150 mL) as the solvent. The crude product was purified by column chromatography (PE/EA= 7:1) to yield compound E5 as a pale yellow oil (279 mg, yield 13.9%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 5.94-5.64 (m, 5H), 5.32-4.91 (m, 10H), 4.49-4.17 (m, 10H), 2.48 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.14, 164.54, 163.80, 138.20, 133.66, 133.55, 133.36, 133.12, 130.80, 130.57, 117.86, 117.46, 65.97, 65.65, 65.34, 32.88, 32.56, 32.47. HRMS (ESI) (m/z): $[M+H]^+$ calcd for $[C_{31}H_{36}O_{10}Na]^+$, 591.2201; found, 591.2189.

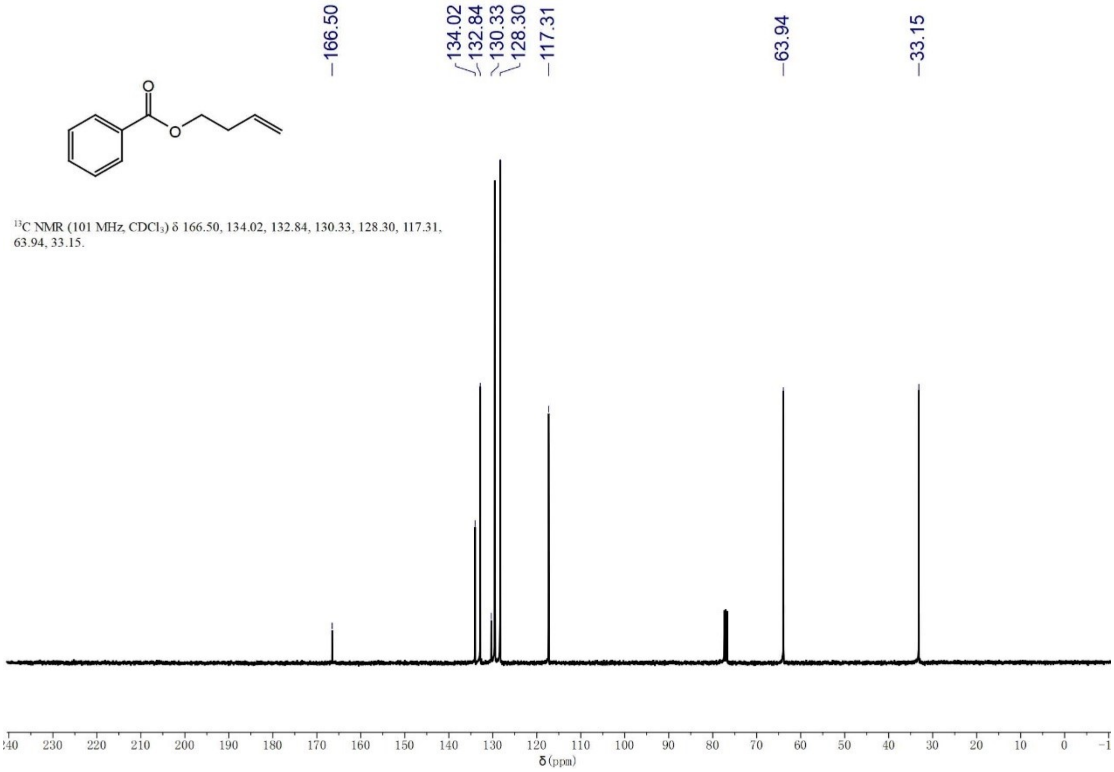
Synthesis of copolymers P1-P5

Copolymers P1-P5 were synthesized according to reported methods[1]. CADs (0.28 mmol, 1 eq) were added to a mixture of acrylamide (1.00 g, 14.06 mmol, 50 eq) and AIBN (16.4 mg) in a 10 mL Schlenk tube. N, N-Dimethylformamide (DMF, 5 mL) was used as the solvent. The reaction mixture was degassed by bubbling argon for 30 minutes to remove oxygen. The polymerization was carried out at 60°C under an argon atmosphere for 12 hours. After the reaction was complete, the mixture was added dropwise to a large excess of anhydrous methanol to precipitate the polymer. The resulting white solid was collected by vacuum filtration and washed with methanol 4-5 times to obtain white polymer powder. The polymer powder was then dried in an infrared drying oven for 4-6 hours.



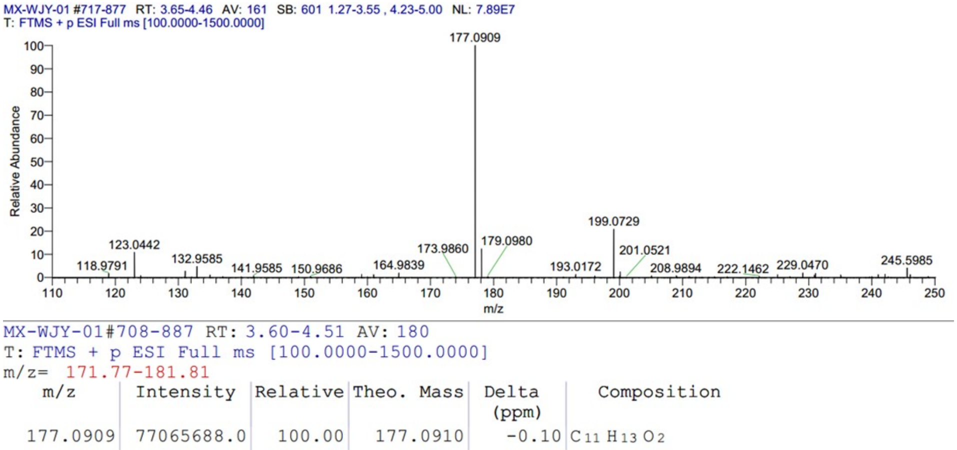
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 5.88 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.26 – 5.02 (m, 2H), 4.38 (t, J = 6.7 Hz, 2H), 2.53 (q, J = 6.7 Hz, 2H).

Fig. S1 The ^{1}H NMR spectrum of E1 in $CDCl_3$.



^{13}C NMR (101 MHz, $CDCl_3$) δ 166.50, 134.02, 132.84, 130.33, 128.30, 117.31, 63.94, 33.15.

Fig. S2 The ^{13}C NMR spectrum of E1 in $CDCl_3$.



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MX-WJY-01 #717-877  RT: 3.65-4.46  AV: 161  SB: 601  1.27-3.55 , 4.23-5.00  NL: 7.89E7
T: FTMS + p ESI Full ms [100.0000-1500.0000]
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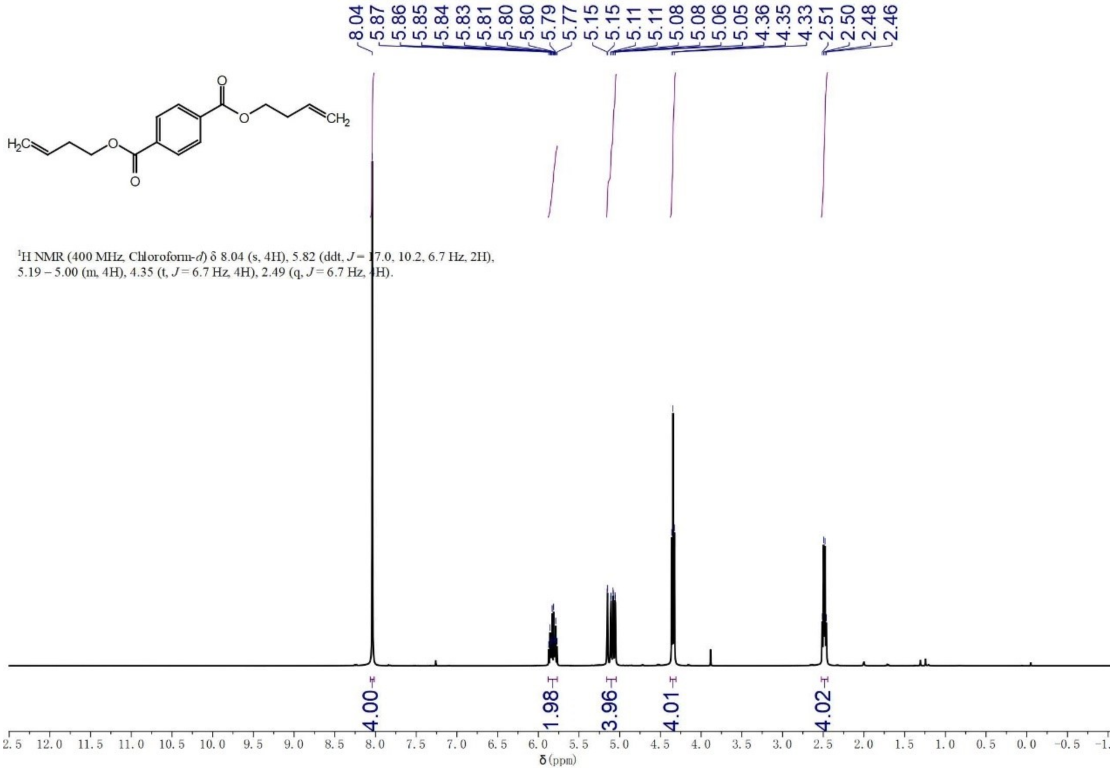
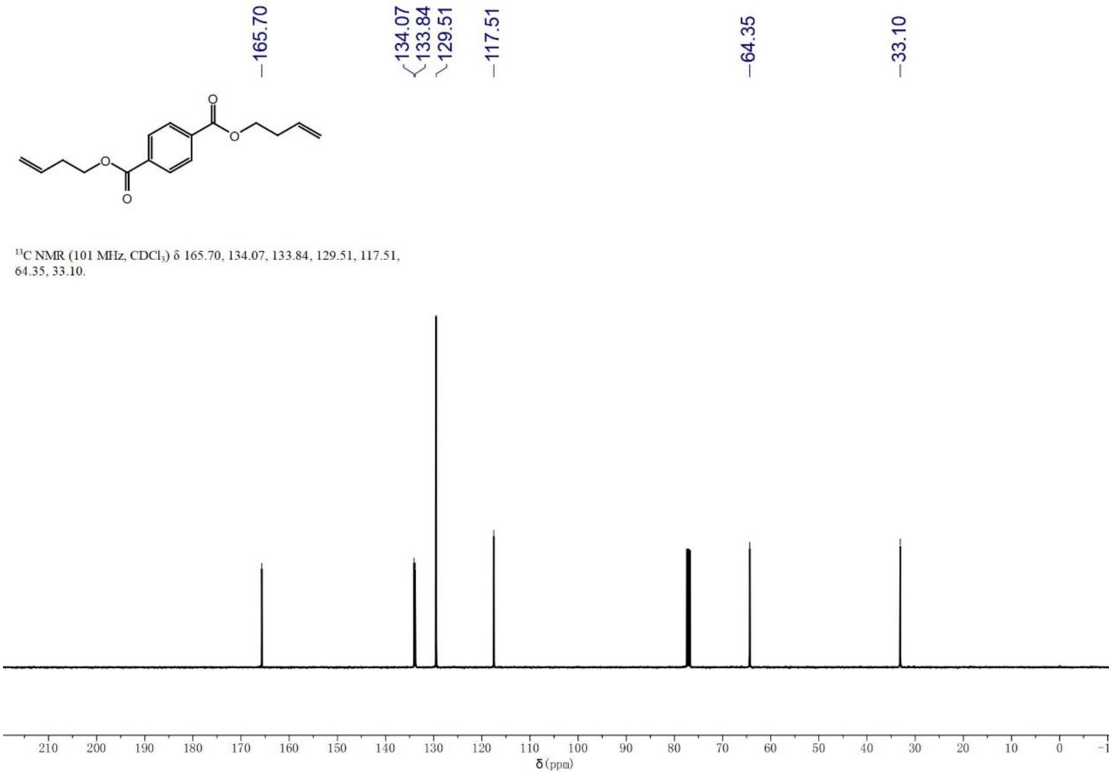
MX-WJY-01#708-887 RT: 3.60-4.51 AV: 180
T: FTMS + p ESI Full ms [100.0000-1500.0000]
m/z= 171.77-181.81
   m/z      Intensity  Relative Theo. Mass  Delta     Composition
                                            (ppm)
 177.0909  77065688.0   100.00   177.0910   -0.10 C11 H13 O2
```

Fig. S3 The ESI-HRMS of E1.



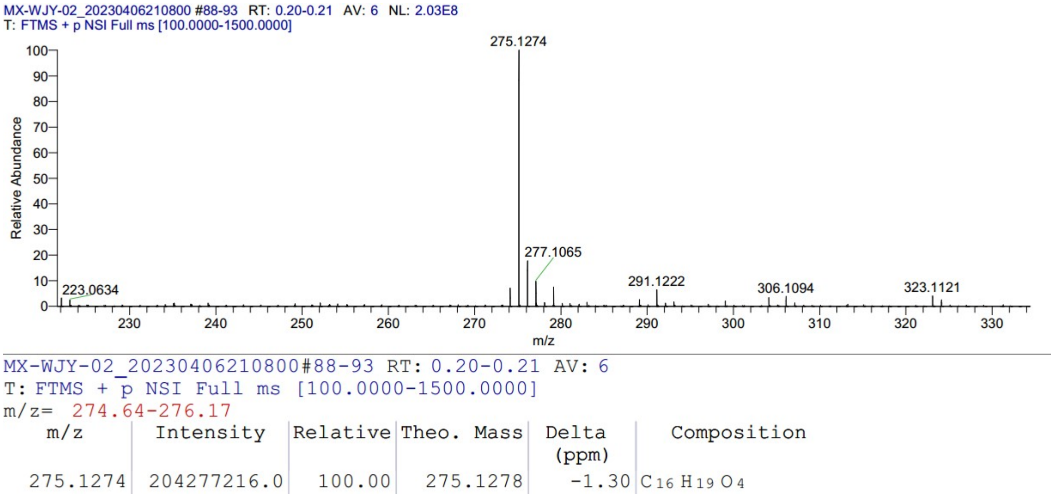
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 4H), 5.82 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 5.19 – 5.00 (m, 4H), 4.35 (t, *J* = 6.7 Hz, 4H), 2.49 (q, *J* = 6.7 Hz, 4H).

Fig. S4 The ^{1}H NMR spectrum of E2 in $CDCl_3$.



^{13}C NMR (101 MHz, $CDCl_3$) δ 165.70, 134.07, 133.84, 129.51, 117.51, 64.35, 33.10.

Fig. S5 The ^{13}C NMR spectrum of E2 in $CDCl_3$.



```
MX-WJY-02_20230406210800#88-93 RT: 0.20-0.21 AV: 6
T: FTMS + p NSI Full ms [100.0000-1500.0000]
m/z= 274.64-276.17
    m/z    |  Intensity   |Relative|Theo. Mass| Delta  |   Composition
           |              |        |          | (ppm)  |
  275.1274 | 204277216.0  | 100.00 | 275.1278 |  -1.30 |C16 H19 O4
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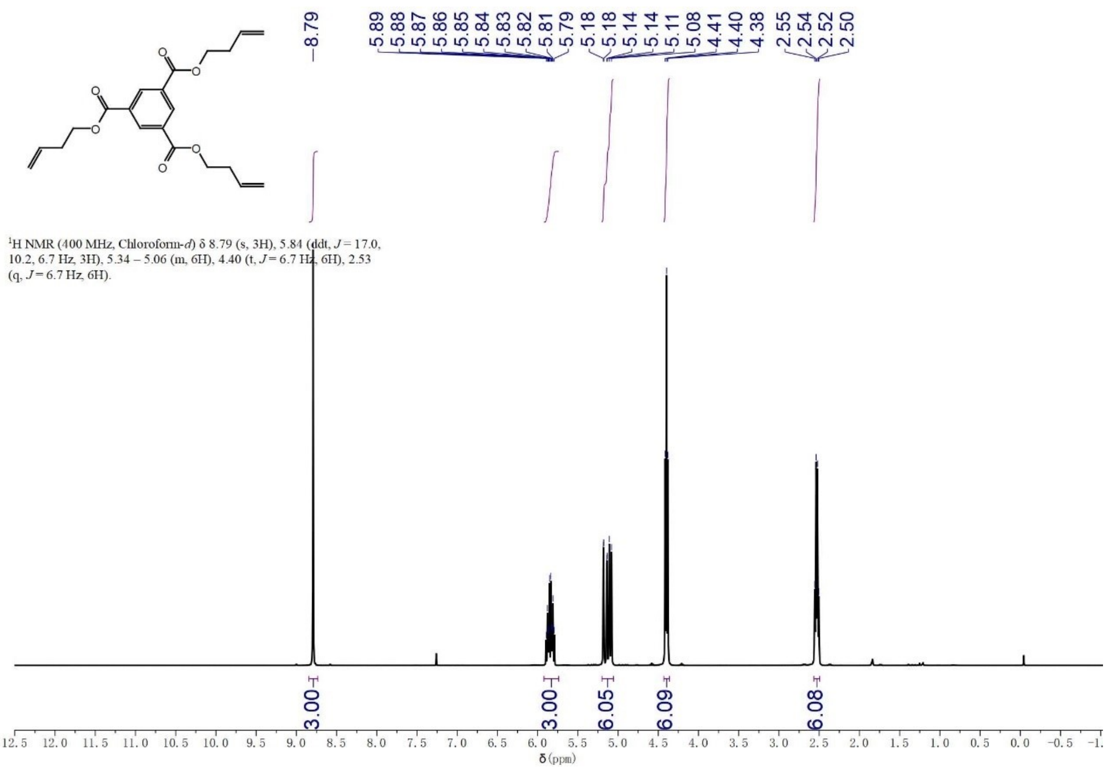
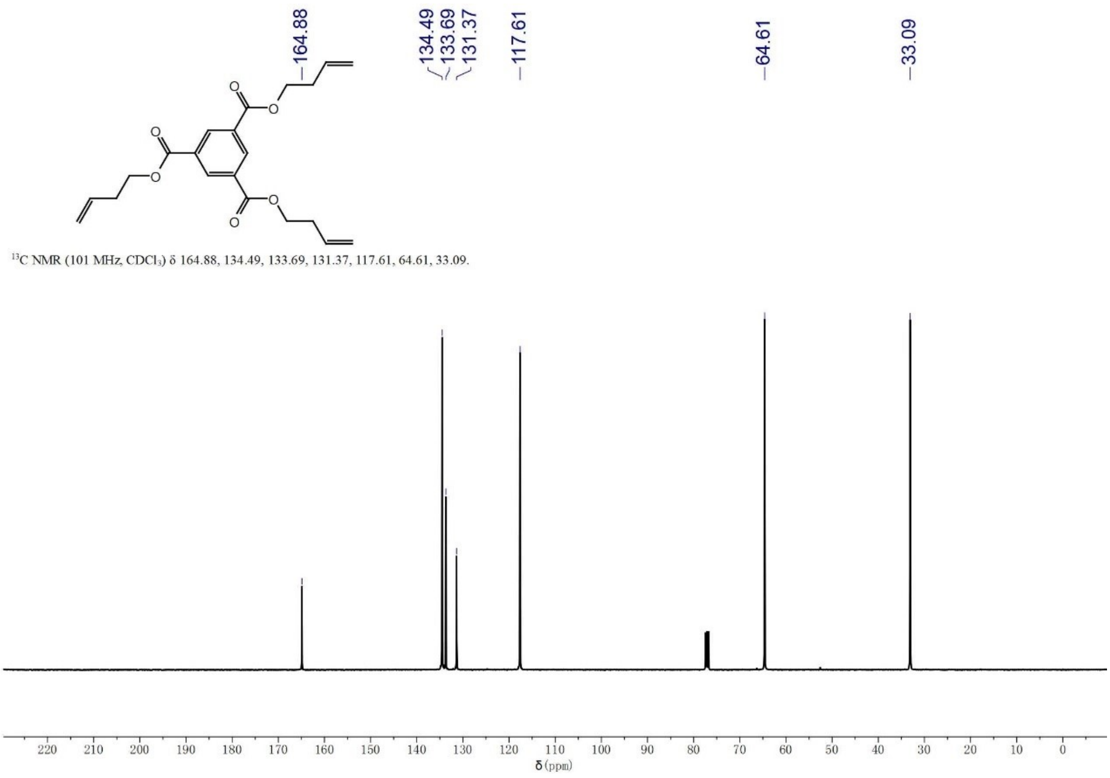
Fig. S6 The DART-HRMS of E2.



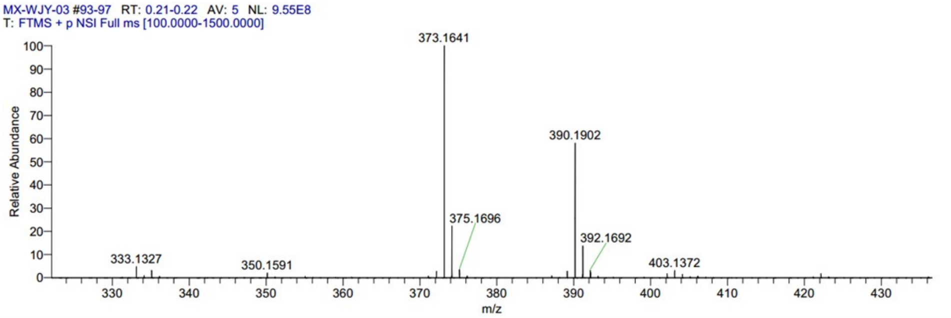
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (s, 3H), 5.84 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 3H), 5.34 – 5.06 (m, 6H), 4.40 (t, *J* = 6.7 Hz, 6H), 2.53 (q, *J* = 6.7 Hz, 6H).

Fig. S7 The ^{1}H NMR spectrum of E3 in $CDCl_3$.



^{13}C NMR (101 MHz, $CDCl_3$) δ 164.88, 134.49, 133.69, 131.37, 117.61, 64.61, 33.09.

Fig. S8 The ^{13}C NMR spectrum of E3 in $CDCl_3$.



```
MX-WJY-03#93-97 RT: 0.21-0.22 AV: 5
T: FTMS + p NSI Full ms [100.0000-1500.0000]
m/z= 372.32-374.17
   m/z      Intensity    Relative Theo. Mass  Delta      Composition
                                              (ppm)
 373.1641  955390080.0    100.00   373.1646   -1.27 C21 H25 O6
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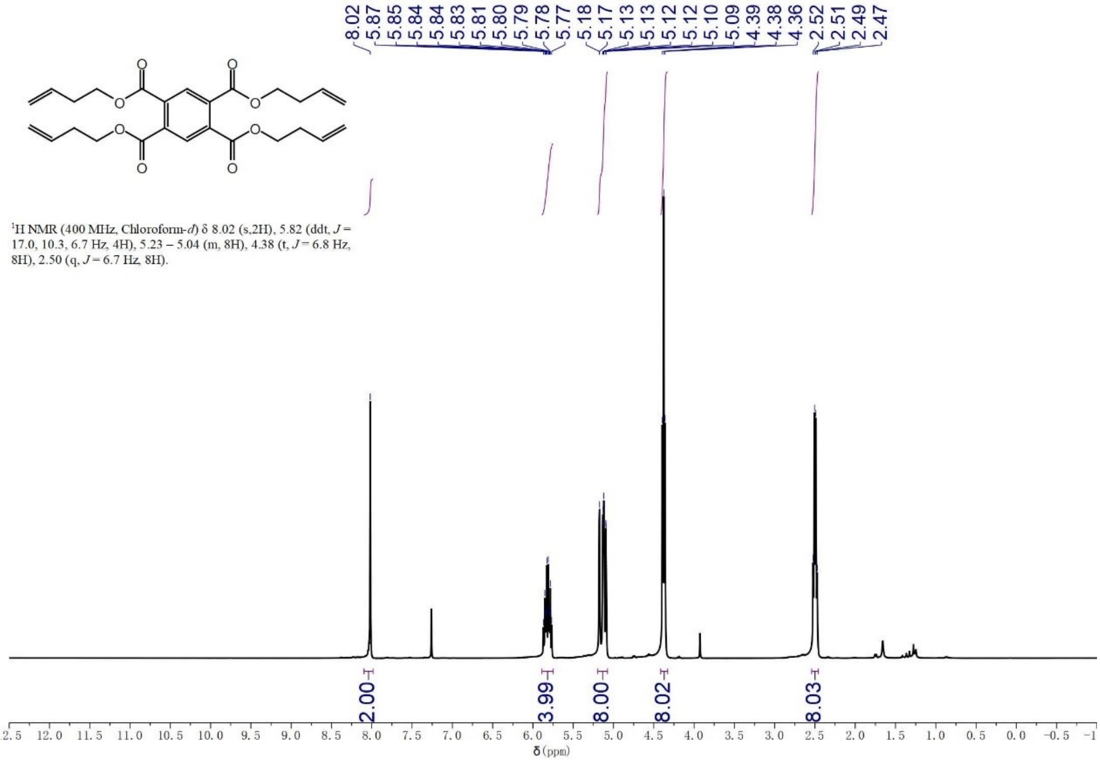
Fig. S9 The DART-HRMS of E3.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s,2H), 5.82 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 4H), 5.23 – 5.04 (m, 8H), 4.38 (t, *J* = 6.8 Hz, 8H), 2.50 (q, *J* = 6.7 Hz, 8H).

Fig. S10 The ^{1}H NMR spectrum of E4 in $CDCl_3$.

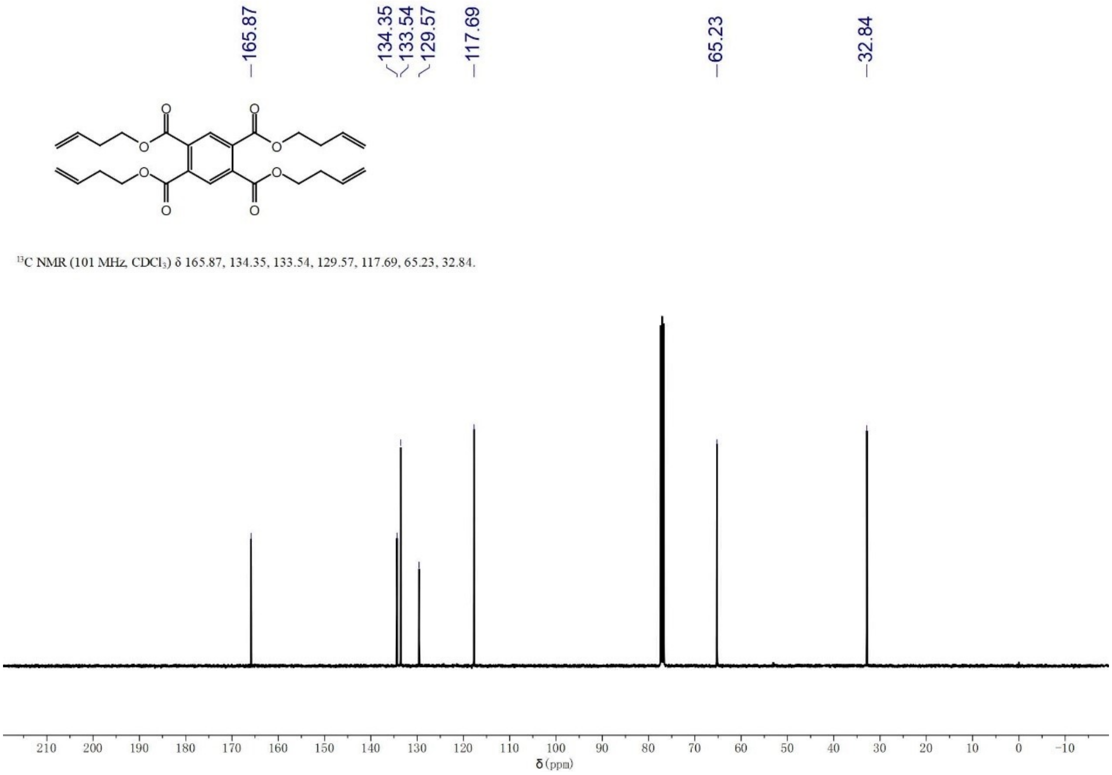
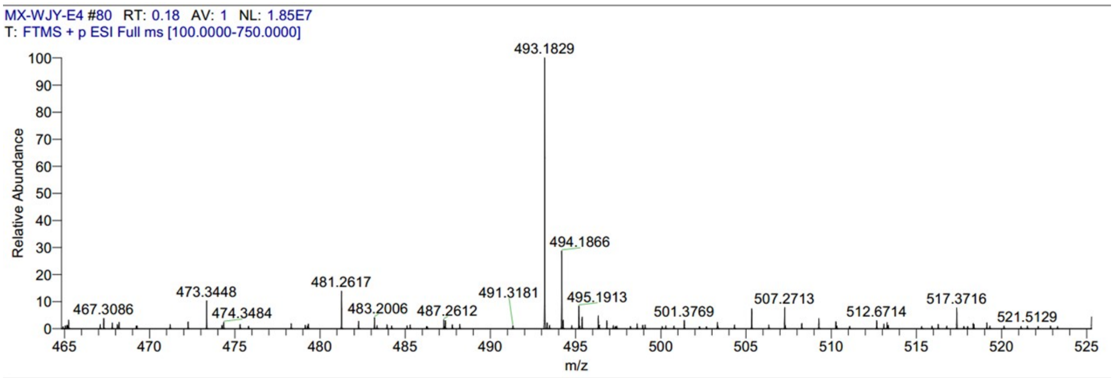
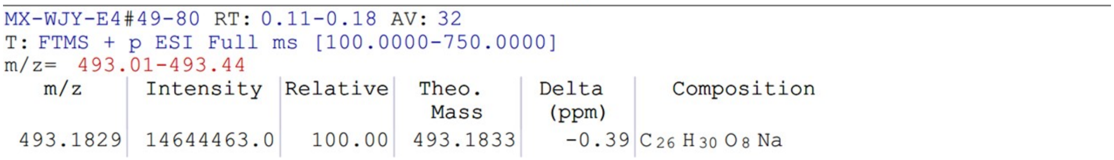


Fig. S11 The ^{13}C NMR spectrum of E4 in CDCl$_3$.





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MX-WJY-E4#49-80 RT: 0.11-0.18 AV: 32
T: FTMS + p ESI Full ms [100.0000-750.0000]
m/z= 493.01-493.44
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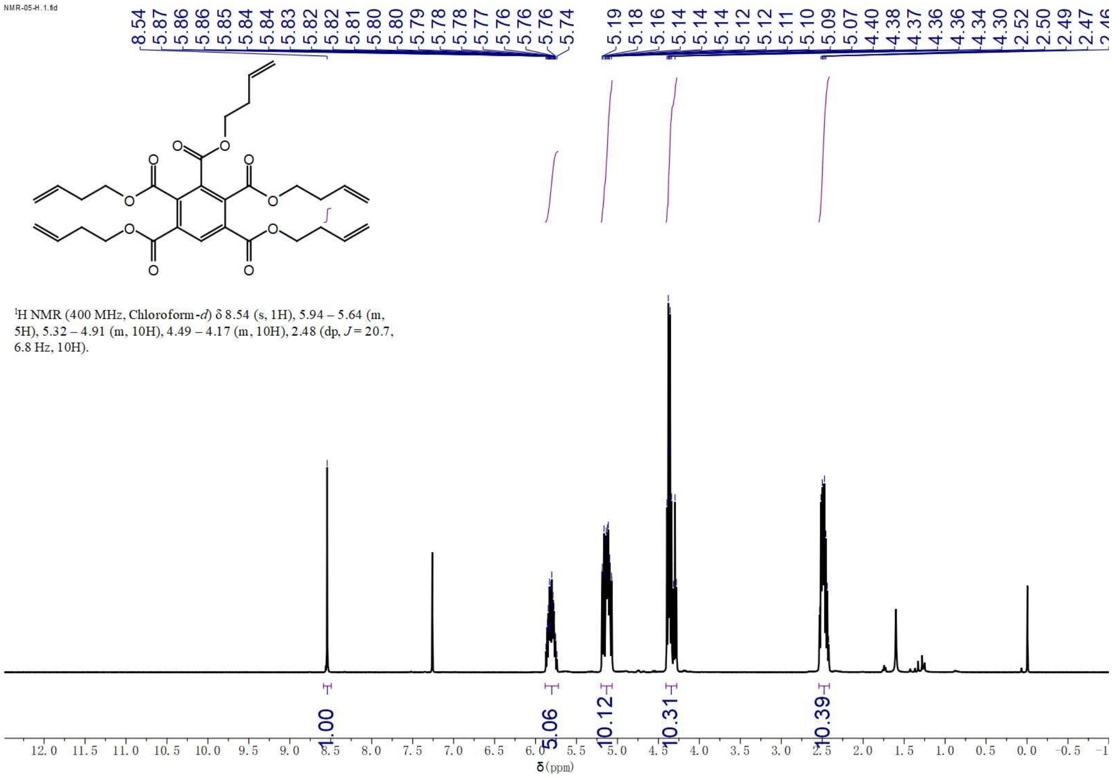
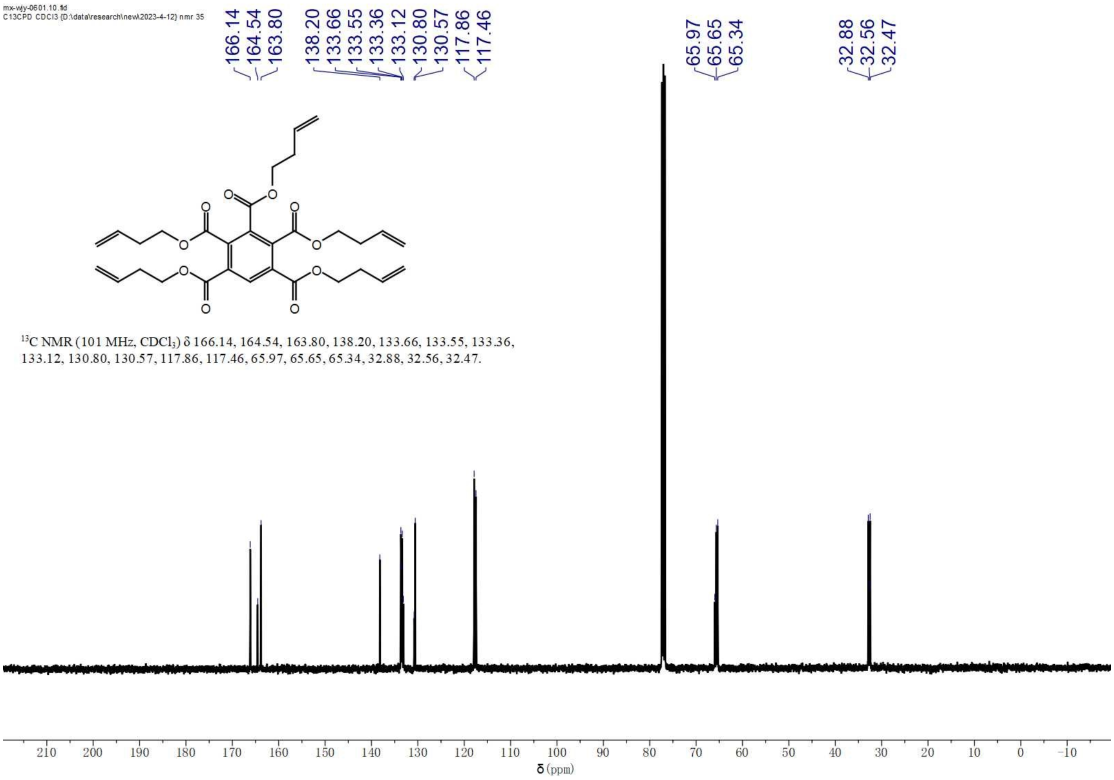
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
493.1829	14644463.0	100.00	493.1833	-0.39	C 26 H 30 O 8 Na

Fig. S12 The ESI-HRMS of E4.



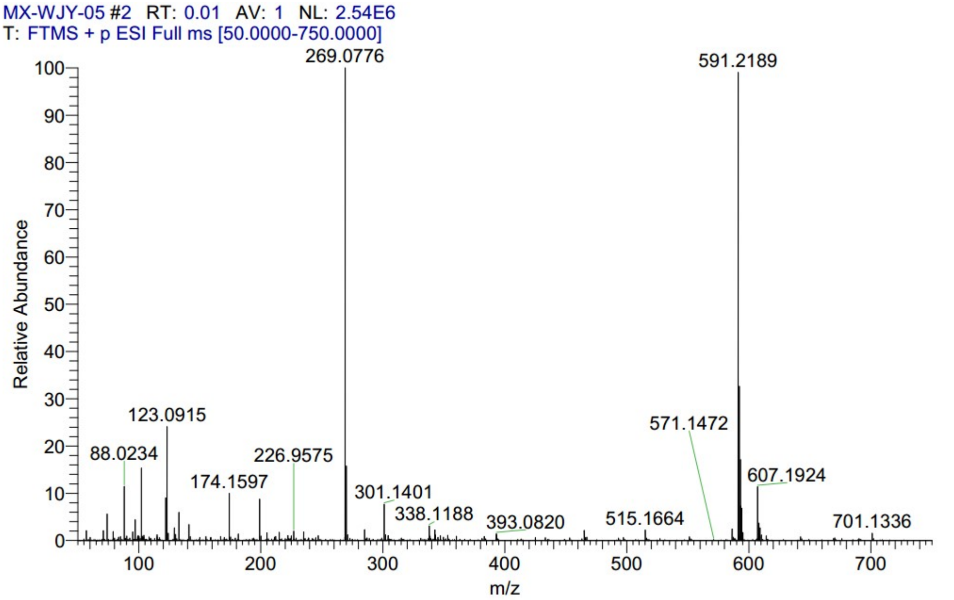
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 5.94 – 5.64 (m, 5H), 5.32 – 4.91 (m, 10H), 4.49 – 4.17 (m, 10H), 2.48 (dp, *J* = 20.7, 6.8 Hz, 10H).

Fig. S13 The ^{1}H NMR spectrum of E5 in $CDCl_3$.



^{13}C NMR (101 MHz, $CDCl_3$) δ 166.14, 164.54, 163.80, 138.20, 133.66, 133.55, 133.36, 133.12, 130.80, 130.57, 117.86, 117.46, 65.97, 65.65, 65.34, 32.88, 32.56, 32.47.

Fig. S14 The ^{13}C NMR spectrum of E5 in $CDCl_3$.



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MX-WJY-05#2 RT: 0.01
T: FTMS + p ESI Full ms [50.0000-750.0000]
m/z= 588.11-593.54
   m/z    | Intensity |Relative| Theo.  | Delta  |    Composition
          |           |        |  Mass  | (ppm)  |
 591.2189 | 2640950.3 | 100.00 |591.2201|   -1.20|C 31 H 36 O 10 Na
```

Fig. S15 The ESI-HRMS of E5.

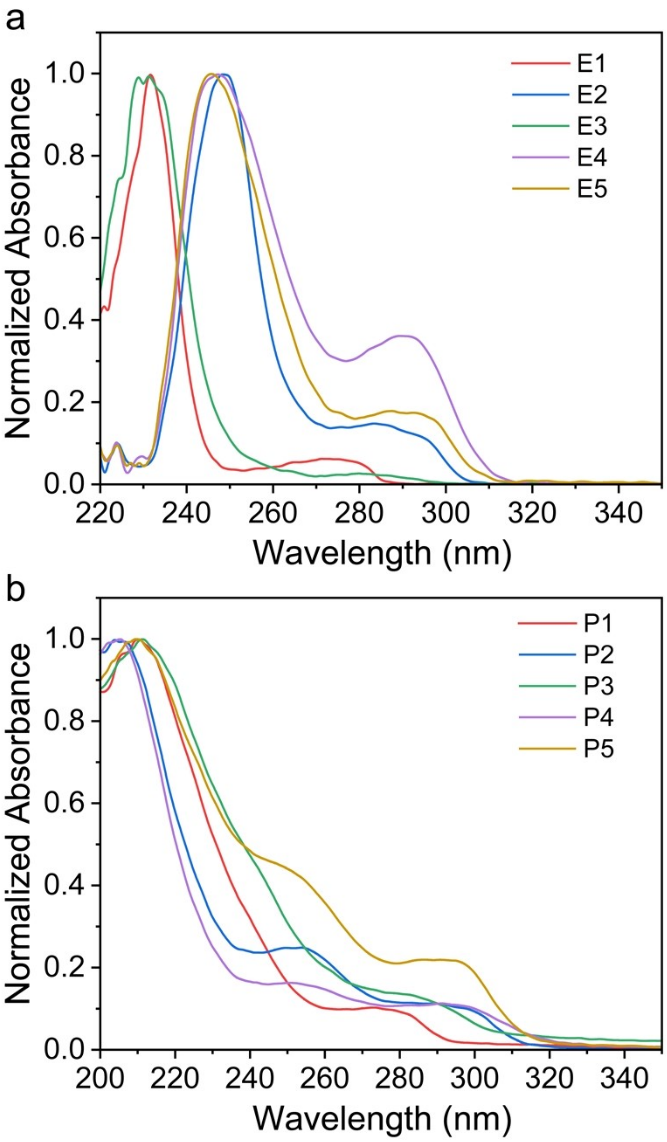

Fig. S16 Normalized absorbance of (a) E1-E5 in 1,4-dioxane (10^{-4}M) and (b) P1-P5.

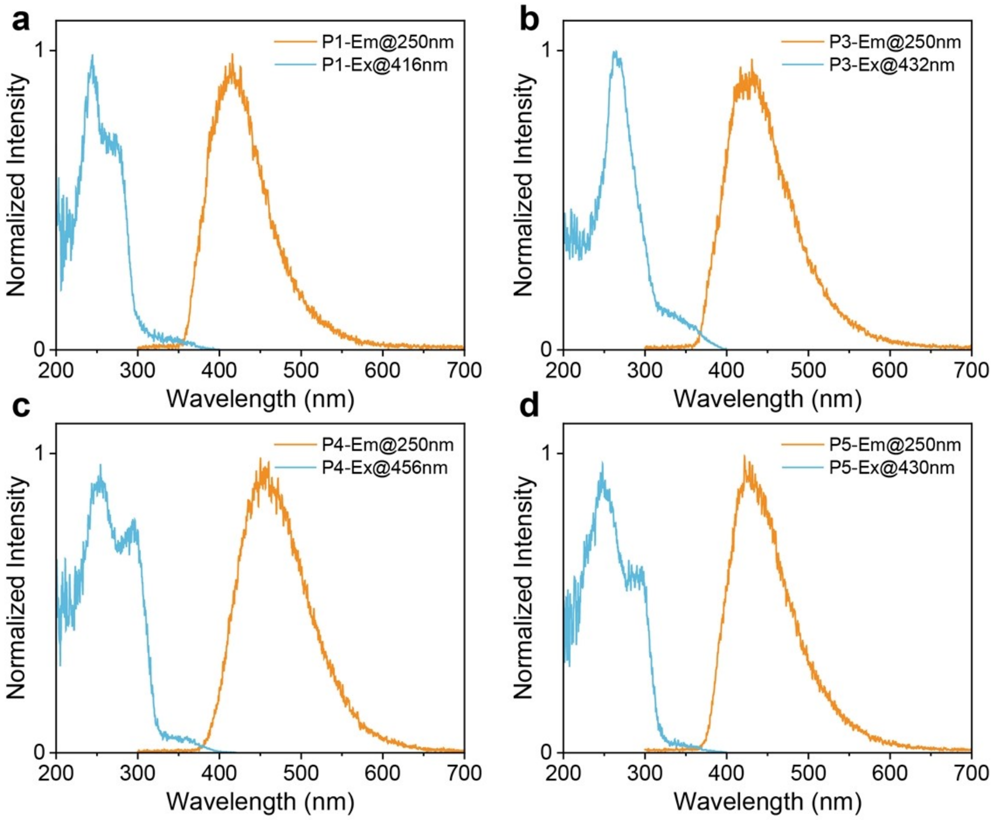

Fig. S17 Deley emission and excitation spectra of (a) P1 (b) P3 (c) P4 and (d) P5 at room temperature.

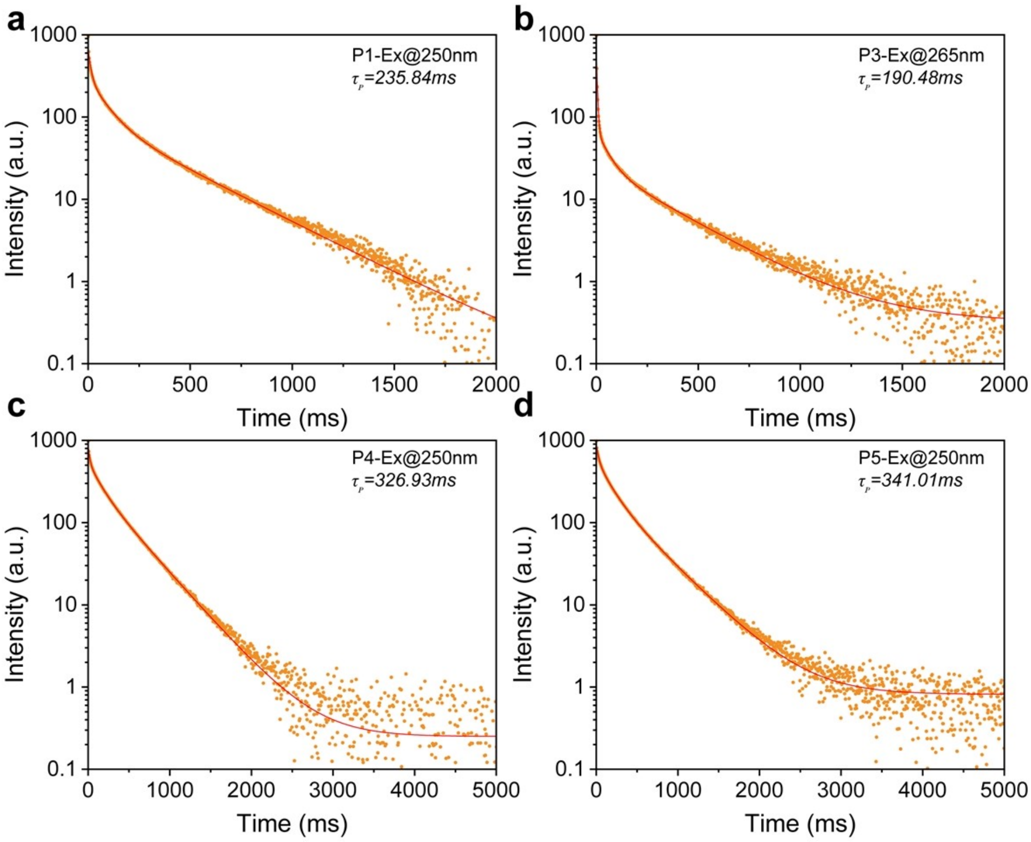

Fig. S18 Deley decay curves of (a) P1 (b) P3 (c) P4 and (d) P5 at room temperature.

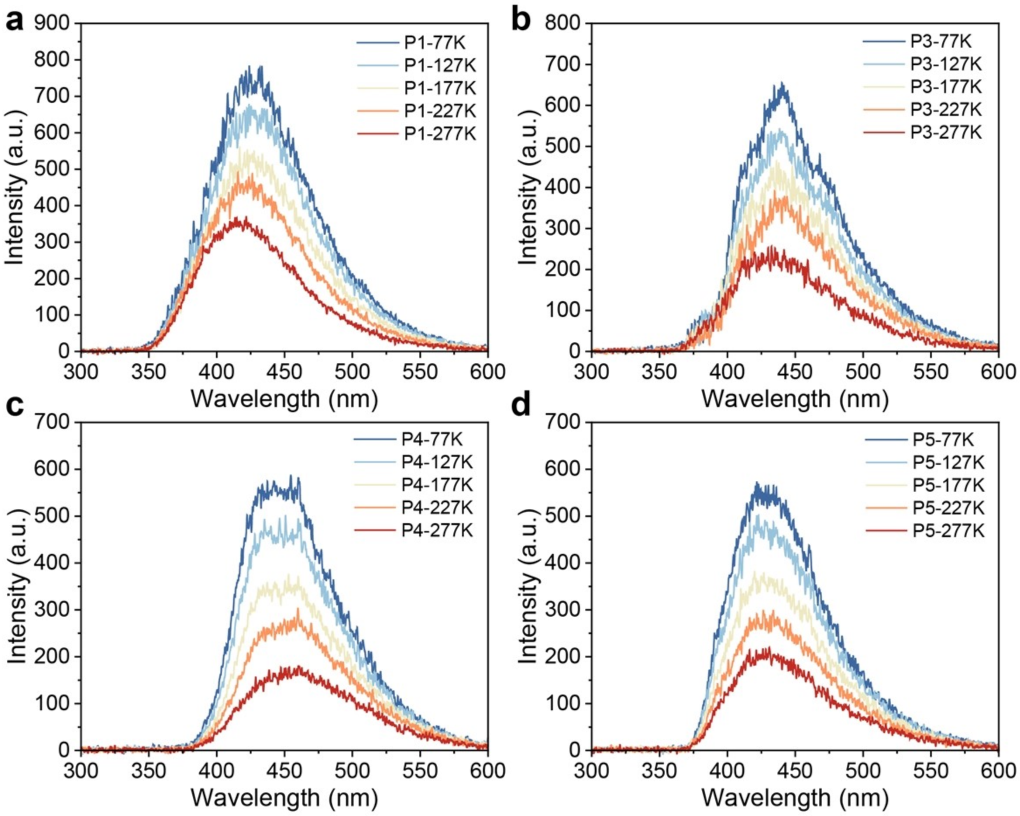

Fig. S19 Deley emission and excitation spectra of (a) P1 (b) P3 (c) P4 and (d) P5 from 77K to 277K.

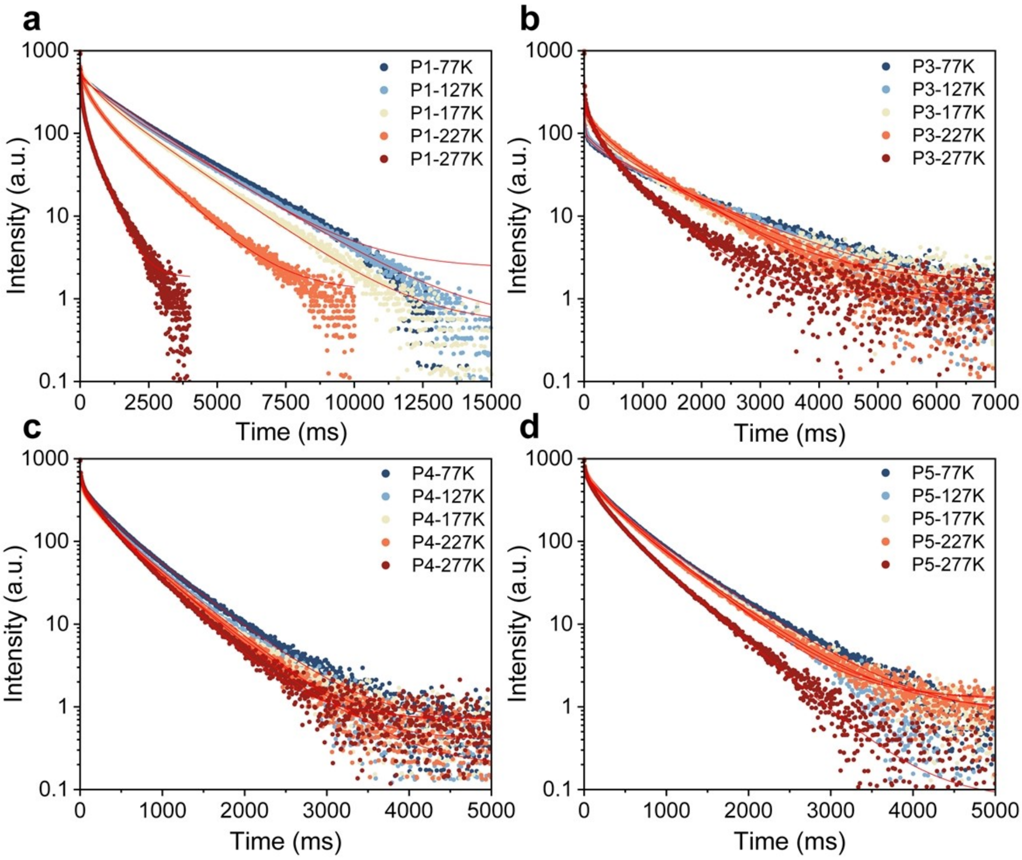

Fig. S20 Deley decay curves of (a) P1 (b) P3 (c) P4 and (d) P5 from 77K to 277K.

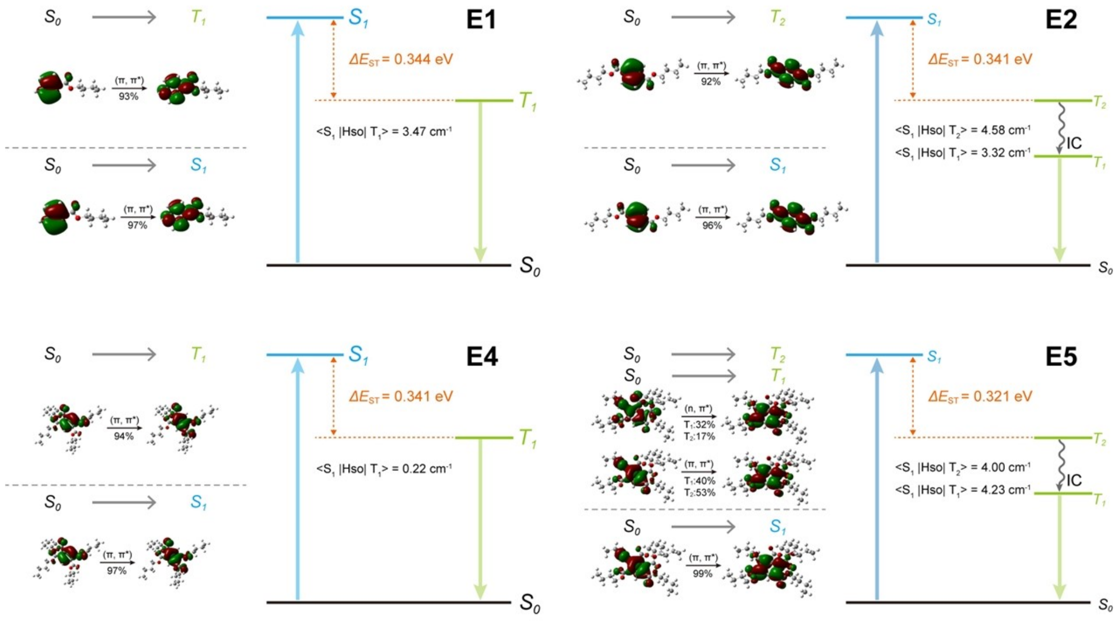

Fig. S21 Theoretical calculation results of (a) E1, (b) E2, (c) E4 and (d) E5 including excited-state electronic transitions, ΔE_{ST} and SOC values.

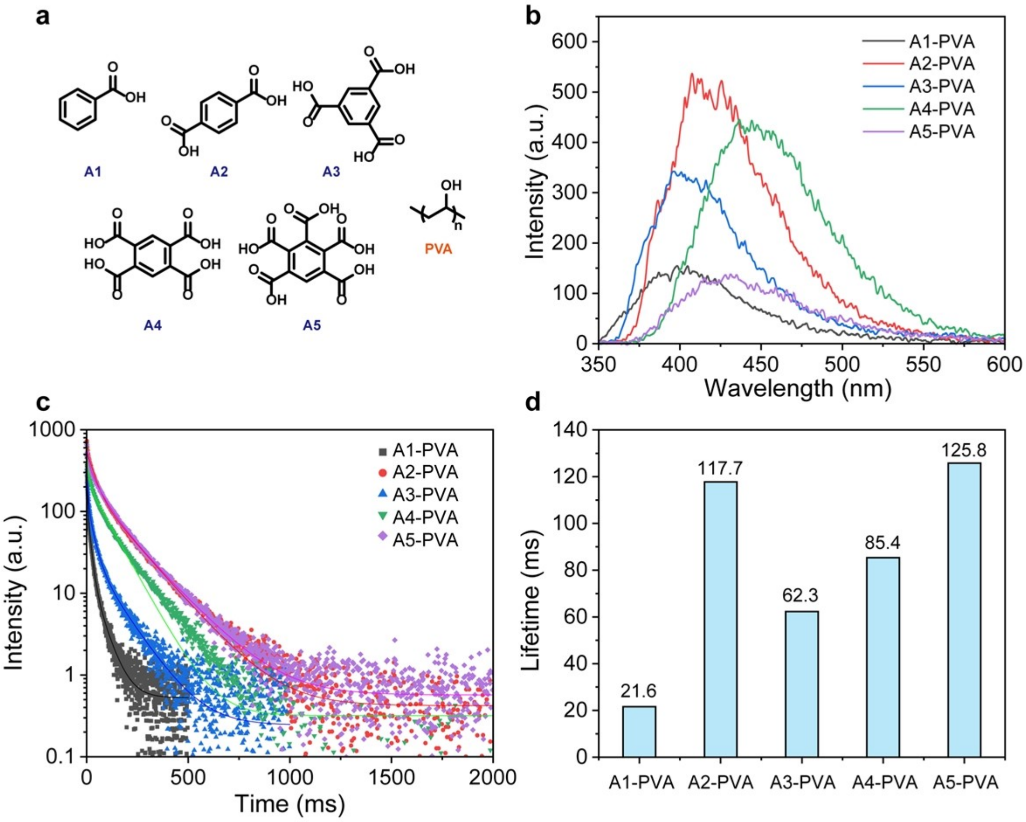

Fig. S22 (a) Chemical structures of A1-A5 and PVA; (b) Delayed emission spectra (delay time = 0.2 ms), (c) decay curves and (d) fitted lifetimes of A1-PVA to A5-PVA.

Table S1 Characterizations of P1-P5.

Sample	P1	P2	P3	P4	P5
Mw	56710	45120	72541	15532	39168
Mn	19790	28350	41497	8417	27353
PDI	2.866	1.592	1.748	1.845	1.432

Table S2 Photophysical characterizations of P1-P5.

	P1	P2	P3	P4	P5
Afterglow duration/s	1.76	4.64	1.74	2.42	2.78
Phosphorescent quantum yield (Φ_{P})/%	6.3	8.9	5.1	8.2	8.8
CIE coordinates	(0.161,0.086)	(0.161,0.110)	(0.163,0.118)	(0.164,0.180)	(0.163,0.117)

Table S3 Fitted lifetimes from delayed decay curves at different temperatures of P1-P5.

	77K	127K	177K	227K	277K	298K
P1/ms	2125.34	1947.80	1593.67	1142.21	452.50	235.84
P2/ms	1410.84	1351.36	1255.02	1090.70	705.55	553.42
P3/ms	1180.64	1146.69	851.64	838.35	490.30	190.48
P4/ms	493.49	471.30	449.65	432.03	386.26	326.93
P5/ms	551.31	539.33	524.63	493.74	409.77	341.01

Table S4 The energy levels and transition configurations of singlet and triplet excited states of E1-E5 in gas phase revealed by TD-DFT calculation.

	S_1	T_1	T_2	T_3	T_4	T_5
E1	2.628 eV H→L 97.1%	2.284 eV H→L 92.8%	2.797 eV H-1→L 91.0%	3.725 eV H-2→L 96.9%	4.042 eV H-3→L 73.3%, H-4→L 7.8%	4.429 eV H-2→L+1 34.4%, H-4→L 27.5%, H-3→L 18.3%
E2	3.239 eV H→L 96.3%	2.673 eV H-1→L 91.7%	2.898 eV H→L 92.4%, H→L+2 6.1%	3.510 eV H-2→L 94.9%	3.695 eV H-4→L 82.0%	3.835 eV H-3→L 90.6%, H-3→L+2 7.8%

E3	4.437 eV H→L+1 44.3%, H-1→L 43.6%, H→L 5.7%, H-1→L+1 5.6%	3.085 eV H→L 43.8%, H-1→L+1 39.6%, H→L+1 5.6%, H-1→L 5.1%	3.867 eV H→L+1 56.4%, H-1→L 40.3%	3.871 eV H-1→L+1 49.6%, H→L 46.9%	4.187 eV H-3→L+1 46.1%, H-2→L 33.2%, H-4→L+2 7.9%	4.210 eV H-1→L 51.9%, H→L+1 35.2%, H-1→L+1 6.7%
E4	1.617 eV H→L 97.4%	1.358 eV H→L 93.9%	2.691 eV H-1→L 67.2%, H-2→L 12.1%	2.713 eV H→L+1 86.4%, H-6→L 5.1%	3.290 eV H-2→L 73.2%, H-1→L 9.6%, H-5→L 5.5%	3.560 eV H-3→L 77.0%, -5→L 5.4%, H-1→L 5.2%
E5	2.723 eV H→L 98.9%	2.402 eV H→L 40.3%, H-2→L 32.4%, H-4→L 11.3%, H-1→L 6.3%	2.645 eV H→L 52.9%, H-2→L 17.0%, H-1→L 10.3%, H-3→L 10.2%	3.173 eV H-1→L 63.5%, H-2→L 14.8%, H-4→L 8.0%	3.333 eV H-3→L 53.2%, H-5→L 13.1%, H-1→L 9.3%, H-4→L 6.8%, H-6→L 5.2%	3.516 eV H-6→L 65.6%, H-4→L 6.3%, H-3→L 5.7%, H-7→L 5.3%

References

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