Electronic Supplementary Information

9,9′-Anthryl-Anthroxy Radicals: Strategic Stabilization for Highly Reactive Phenoxy Radicals

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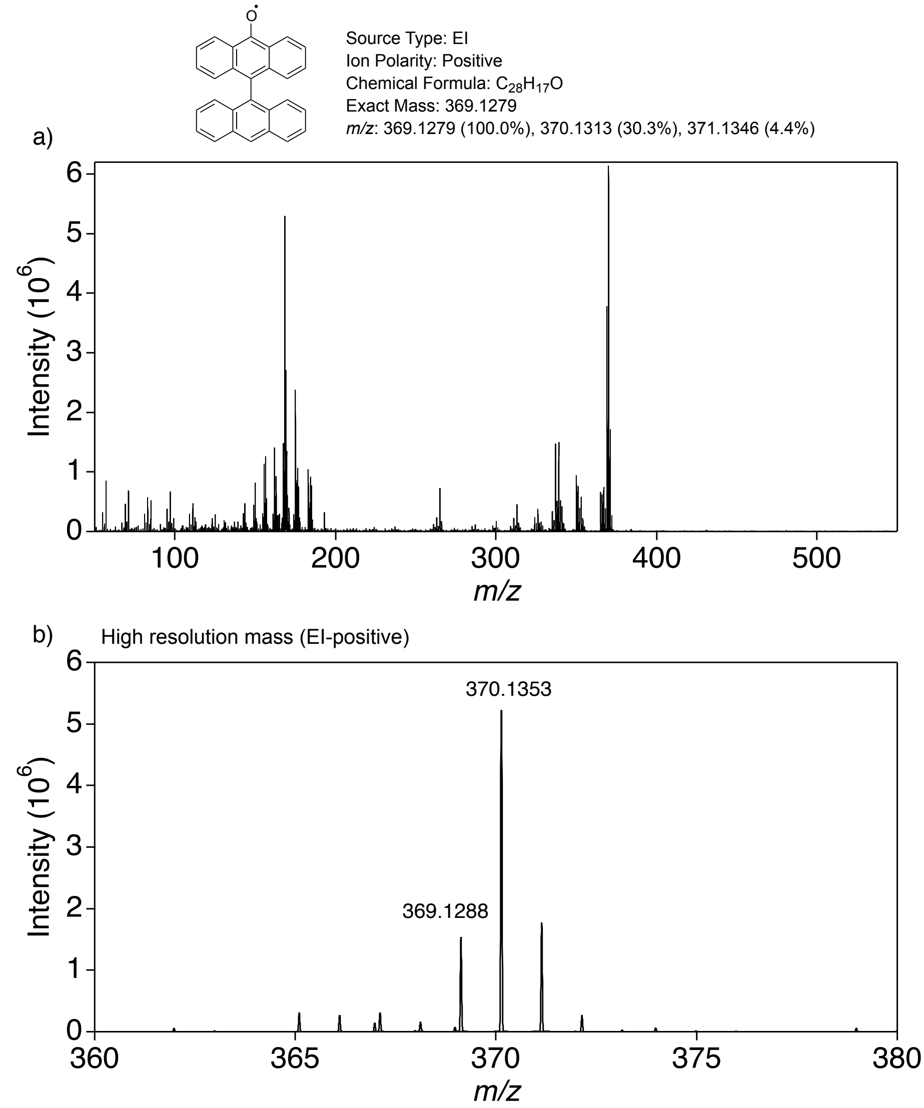
1. Synthesis and general methods

Commercially available reagents and solvents for syntheses were of reagent grade and used without further purification. TLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. For spectral measurements, spectral-grade toluene, dichloromethane, methanol and acetonitrile were purchased from Nacalai Tesque. The dichloromethane used for cyclic voltammetry measurements was distilled from CaH_2.

Compound 1

LAH (0.53 g, 13.4 mmol) was added slowly to suspension of **3** (0.34 g, 0.884 mmol) in dry THF (25 ml) at 0 ºC. After adding, the reaction mixture was refluxed for 2 h. After refluxing, the reaction mixture was cooled to 0 ºC again. 6 N HCl (26 ml) was added to the mixture and refluxed for 1 h again. The precipitate was filtrated off and washed with water and methanol. The product **5** was used in the following reaction without purification because of the instability under ambient conditions. Compound **5** was dissolved in a mixture of dry pyridine (13 ml) and piperidine (0.80 ml, 8.1 mmol). Pyridine-*N*-oxide (0.70 g, 7.36 mmol) and ferrous sulfate heptahydrate (0.060 g, 0.216 mmmol) were added to the resulting solution, and the reaction mixture was heated to 100 ºC under argon atmosphere for 16 h. After cooling, the reaction mixture was mixed with 6 N HCl (20 ml). The precipitate was filtrated off and washed with water and methanol. The crude product was purified by chromatography on silica gel with $CHCl_3$ ($1^{st.}$time, $R_f = 0.42$), $CHCl_3$-hexane ($2^{nd.}$time, ratio = 1:2, $R_f = 0.15$) and $CHCl_3$:hexane = 1:3 ($3^{rd.}$time, ratio = 1:3, $R_f = 0.03$) and gel permeation chromatography ($CHCl_3$) to afford **1** as a black solid (0.043 g, 15% in 2 steps). MS (EI): *m*/*z*: 369 $[M]^+$, 370 $[M+1]^+$; HR-EI *m*/*z* = 369.1288, calcd. for $C_{28}H_{17}O$: 369.1279.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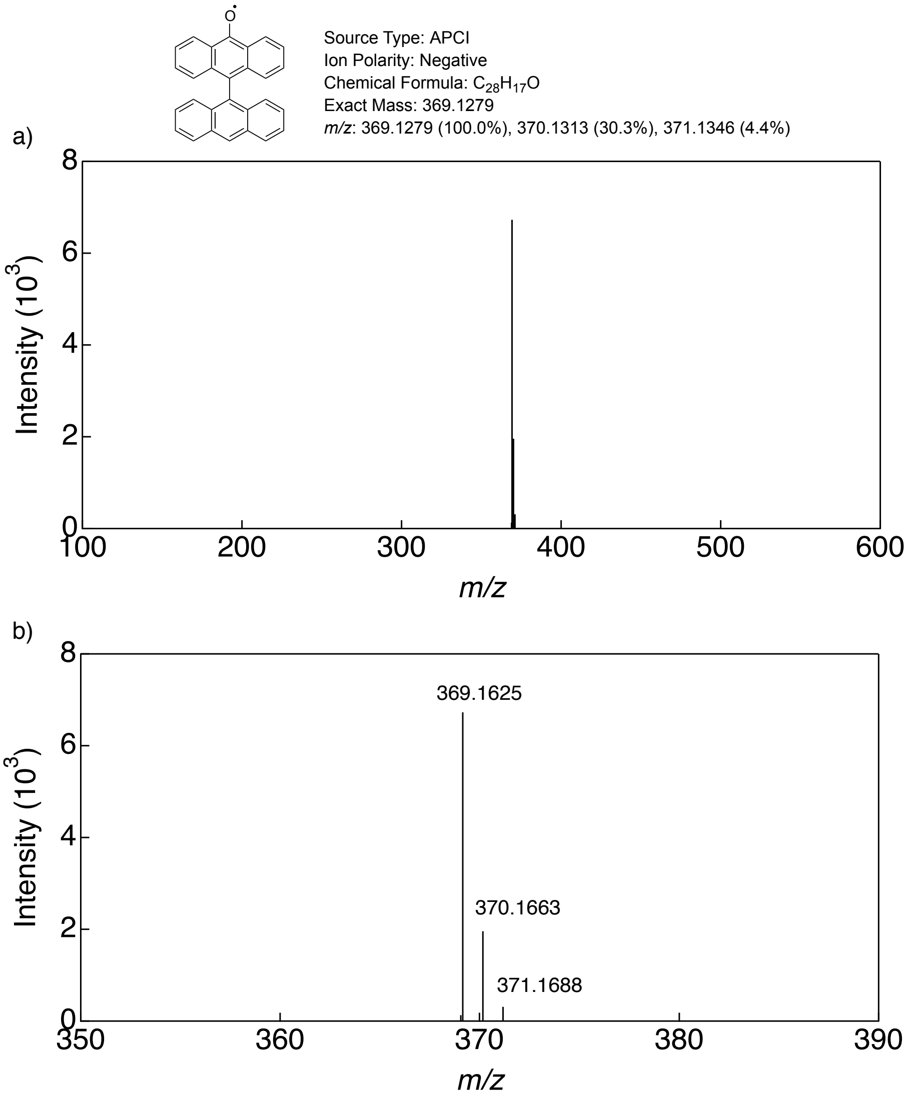
Chemical Formula: $C_{28}H_{17}O$
Exact Mass: 369.1279
m/z: 369.1279 (100.0%), 370.1313 (30.3%), 371.1346 (4.4%)

b) High resolution mass (EI-positive)

Fig. S1 MS spectra (EI, positive) and b) HR-MS of compound **1**.

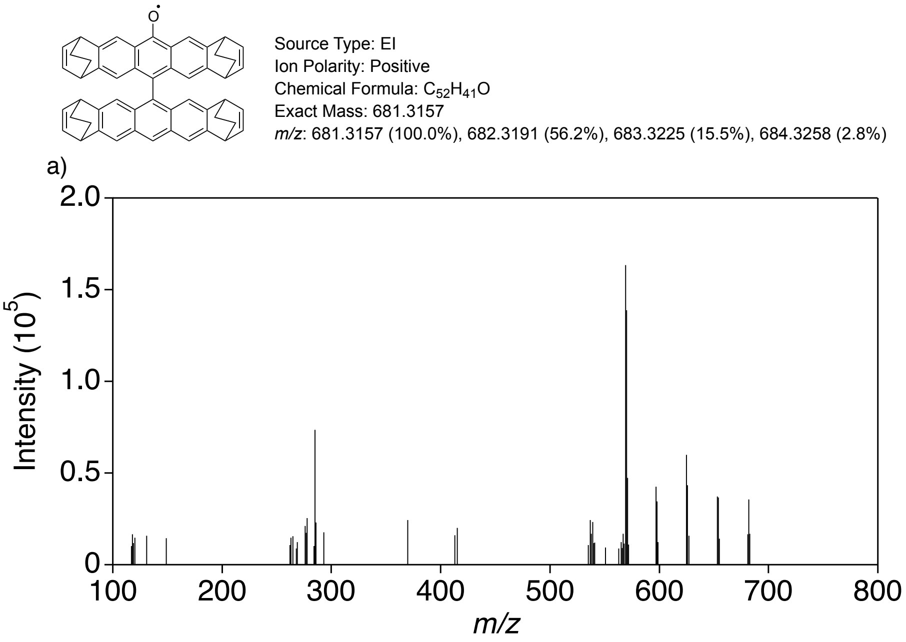


Source Type: APCI
Ion Polarity: Negative
Chemical Formula: $C_{28}H_{17}O$
Exact Mass: 369.1279
m/z: 369.1279 (100.0%), 370.1313 (30.3%), 371.1346 (4.4%)

Fig. S2 MS spectra (APCI, negative) and the expanded chart of compound **1**.

Compound 2

LAH (0.40 g, 10.5 mmol) was added slowly to suspension of **4** (0.40 g, 0.574 mmol) in dry THF (20 ml) at 0 ºC. After adding, the reaction mixture was refluxed for 1 h. After refluxing, the reaction mixture was cooled to 0 ºC again. 6 N HCl (20 ml) was added to the mixture and refluxed for 1 h again. The precipitate was filtrated off and washed with water and methanol. The crude product was purified by chromatography on silica gel with CH_2Cl_2-hexane (4:1) (0.27 g). The product **6** was used in the following reaction without more purification because of the instability under ambient conditions. Compound **6** (0.27 g) was dissolved in a mixture of dry pyridine (20 ml) and piperidine (0.70 ml, 7.09 mmol). Pyridine-*N*-oxide (0.93 g, 0.978 mmol) and ferrous sulfate heptahydrate (0.074 g, 0.266 mmmol) were added to the resulting solution, and the reaction mixture was heated to 100 ºC under argon atmosphere for 4 h. After cooling, the reaction mixture was mixed with 3 N HCl (20 ml). The precipitate was filtrated off and washed with water and methanol. The crude product was purified by chromatography on silica gel with CH_2Cl_2-hexane (ratio; 1:1, $R_f = 0.03$) and recrystallization from CH_2Cl_2–methanol to afford **2** as a black solid (0.074 g, 19% in 2 steps). MS (EI): *m/z*: 681 $[M]^+$, 682 $[M+1]^+$, 653 $[M-28(-C_2H_4)]^+$, 625 $[M-56(-2C_2H_4)]^+$, 597 $[M-84(-3C_2H_4)]^+$, 569 $[M-114(-4C_2H_4)]^+$; HR-EI: *m/z* = 681.3143, calcd. for $C_{52}H_{41}O$: 681.3157.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Ion Polarity: Positive
Chemical Formula: $C_{52}H_{41}O$
Exact Mass: 681.3157
m/z: 681.3157 (100.0%), 682.3191 (56.2%), 683.3225 (15.5%), 684.3258 (2.8%)

b) High resolution mass (EI-positive)

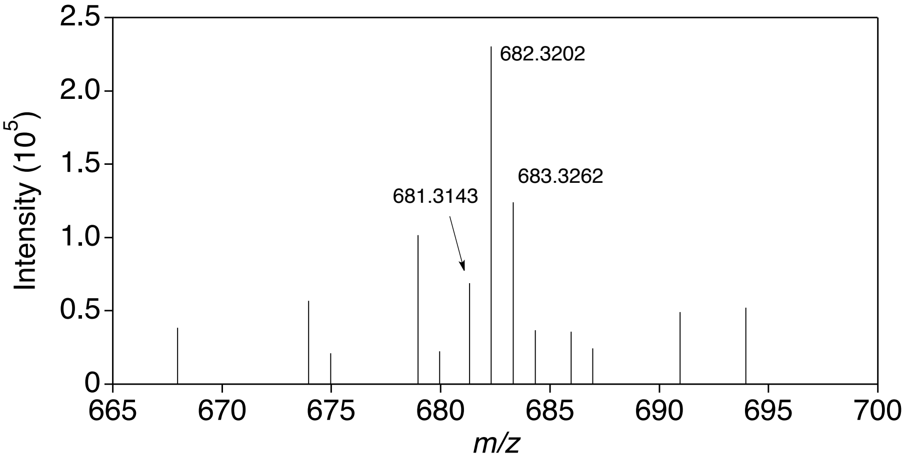

Fig. S3 MS spectra (EI, positive) and b) HR-MS of compound **2**.

General

EI mass spectra were measured on a JEOL JMS-700 MStation spectrometer. UV-vis spectra were measured on a JASCO UV/VIS/NIR Spectro-photometer V-570. ESR spectra were recorded on a JEOL JES-FA100.

X-ray crystallography

X-ray crystallographic data were recorded at 100 K on a Rigaku R-AXIS RAPID/S using Mo-Kα radiation and at 90 K with a BRUKER-APEXII X-Ray diffractometer equipped with a large area CCD detector by using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The diffraction data were processed with Crystal Structure of the Rigaku program, solved with the SIR-97 program and refined with the SHELX-97 program (G. M. Sheldrick, *Acta. Cryst.*, 2008, A64, 112–122).

Cyclic voltammetry measurements

CV measurements were conducted in a solution of 0.1 M *n*-Bu_4NPF_6 in dry dichloromethane with a scan rate of 100 mV/s at room temperature in an argon-filled cell. A glassy carbon electrode and a Pt wire were used as a working and a counter electrode, respectively. An Ag/Ag^+ electrode was used as a reference electrode, which was externally calibrated with the half-wave potential of ferrocene/ferrocenium (Fc/Fc^+) redox couple.

2. Crystallographic data and structure refinement

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{28} H_{17} O$
Formula weight	369.42
Temperature	103(2) K
Wavelength	0.71075 Å
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	a = 11.6165(6) Å
	b = 12.7592(7) Å
	c = 12.4644(6) Å
Volume	1847.44(17) $Å^3$
Z	4
Density (calculated)	1.328 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
$F(000)$	772
Crystal size	0.20 x 0.02 x 0.01 mm^3
Theta range for data collection	3.19 to 25.34°.
Index ranges	$-13 \le h \le 13, -15 \le k \le 15, -15 \le l \le 14$
Reflections collected	24374
Independent reflections	1690 [R(int) = 0.1079]
Completeness to theta = 25.34°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9992 and 0.9844
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1690 / 0 / 136
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0606$, $wR_2 = 0.1378$
R indices (all data)	$R_1 = 0.1043$, $wR_2 = 0.1572$
Largest diff. peak and hole	0.306 and –0.201 e.$Å^{-3}$

Table S2 Crystal data and structure refinement for co-crystal of **1** and **1H**.

Empirical formula	$C_{58.50}\ H_{37.50}\ Cl_{7.50}\ O_2$	
Formula weight	1038.26	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 11.5782(3) Å	α = 96.3005(8)°
	b = 14.3354(5) Å	β = 101.7870(11)°
	c = 16.4867(5) Å	γ = 113.7045(8)°
Volume	2395.88(13) Å^3	
Z	2	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	0.488 mm^{-1}	
F(000)	1064	
Crystal size	0.12 x 0.10 x 0.08 mm^3	
Theta range for data collection	3.05 to 25.35°	
Index ranges	$-13 \le h \le 13, -17 \le k \le 17, -19 \le l \le 19$	
Reflections collected	34238	
Independent reflections	8742 [*R*(int) = 0.0539]	
Completeness to theta = 25.35°	99.6%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9620 and 0.9438	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8742 / 0 / 667	
Goodness-of-fit on F^2	1.070	
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0507, wR_2 = 0.1220	
R indices (all data)	R_1 = 0.0793, wR_2 = 0.1397	
Largest diff. peak and hole	0.708 and –0.546 e.Å^{-3}	

Table S3 Crystal data and structure refinement for crystal of **2**. (Solvents: toluene-MeOH)

Empirical formula	$C_{52}H_{41}O$	
Formula weight	681.85	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.6594(3) Å	
	b = 21.7535(7) Å	β = 100.1230(10)°
	c = 16.0991(4) Å	
Volume	3674.93(18) $Å^3$	
Z	4	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	1444	
Crystal size	0.18 x 0.12 x 0.03 mm^3	
Theta range for data collection	3.08 to 25.35°.	
Index ranges	$-12 \leq h \leq 12, -26 \leq k \leq 26, -19 \leq l \leq 19$	
Reflections collected	51609	
Independent reflections	6705 [R(int) = 0.0515]	
Completeness to theta = 25.35°	99.6%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9979 and 0.9873	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6705 / 0 / 488	
Goodness-of-fit on F^2	1.017	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0646, wR_2 = 0.1708	
R indices (all data)	R_1 = 0.0824, wR_2 = 0.1832	
Largest diff. peak and hole	0.324 and -0.284 e.$Å^{-3}$	

Table S4 Crystal data and structure refinement for co-crystal of **2**. (Solvents: $CHCl_3$-MeOH)

Empirical formula	$C_{57}H_{46}Cl_{15}O$
Formula weight	1278.69
Temperature	103(2) K
Wavelength	0.71075 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.9660(3) Å
	b = 19.5910(4) Å β = 109.3080(10)°.
	c = 21.6636(4) Å
Volume	5593.9(2) Å^3
Z	4
Density (calculated)	1.518 Mg/m^3
Absorption coefficient	0.778 mm^{-1}
F(000)	2604
Crystal size	0.21 x 0.10 x 0.02 mm^3
Theta range for data collection	3.06 to 25.35°.
Index ranges	$-16 \leq h \leq 16, -21 \leq k \leq 23, -26 \leq l \leq 26$
Reflections collected	78378
Independent reflections	10180 [R(int) = 0.0453]
Completeness to theta = 25.35°	99.6 %
Max. and min. transmission	0.9846 and 0.8536
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10180 / 15 / 784
Goodness-of-fit on F^2	1.080
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0967, wR_2 = 0.2708
R indices (all data)	R_1 = 0.1191, wR_2 = 0.2899
Largest diff. peak and hole	1.232 and -0.765 e.Å^{-3}

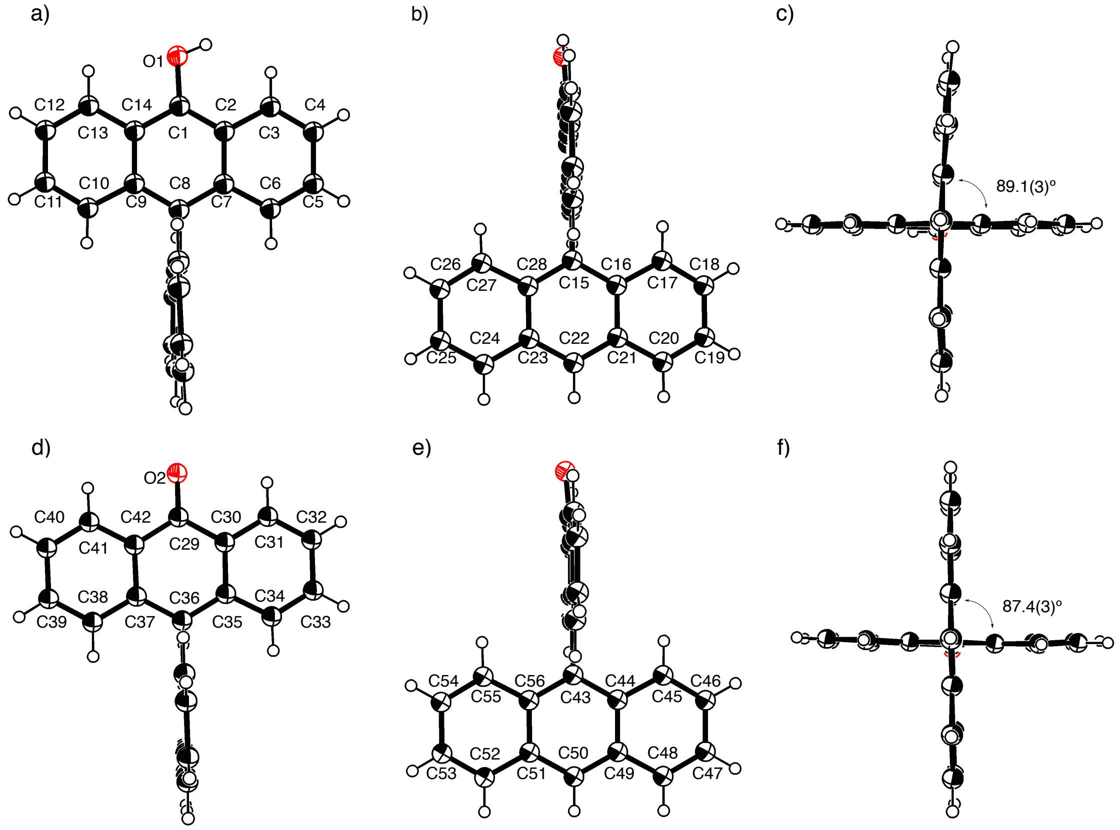

Fig. S4 The numberings of molecular structures of **1-H** (a–c) and **1** (d–f) as co-crystal.

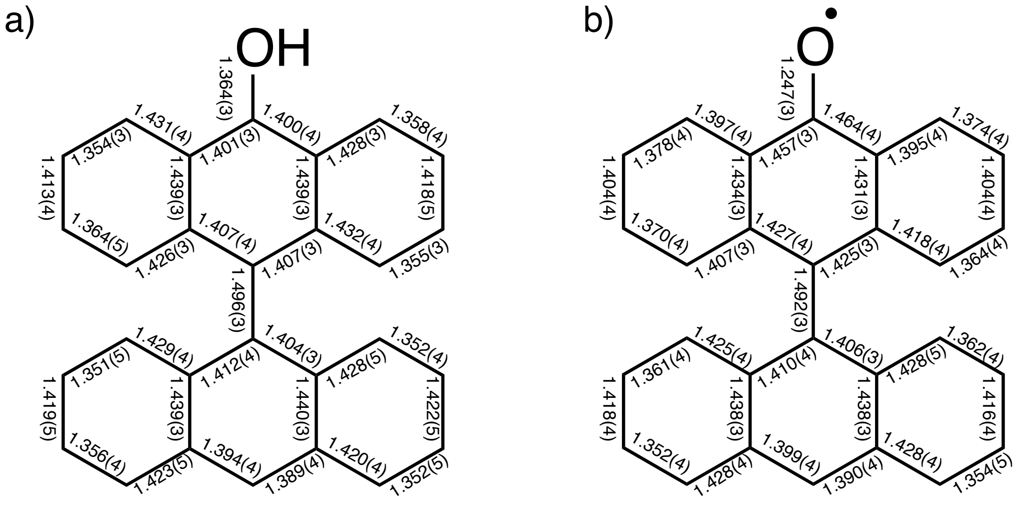

Fig. S5 The details of bond length of a) **1-H** and b) **1** in co-crystal.

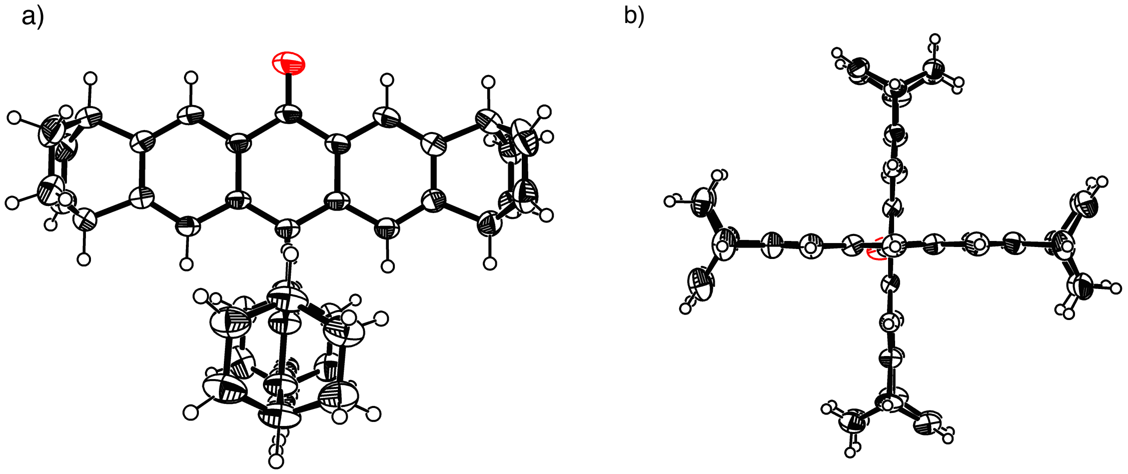

Fig. S6 Crystal structures of a) top view; and b) side view of **2**. (Solvents: $CHCl_3$-MeOH)

3. DFT calculations

The geometries of **1** and **2** were fully optimized using the density functional theory (DFT). The functional and basis set used in the DFT calculations were the Becke's three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP)[1] and the 6-31G(d) basis set,[2] respectively. Equilibrium geometries were verified by the frequency calculations, where no imaginary frequency was found. The excitation energies and oscillator strengths were computed with time-dependent density functional theory (TD-DFT) based on the B3LYP/6-31G(d) optimized geometries. All the calculations were carried out using the Gaussian 09 suite of programs.[3]

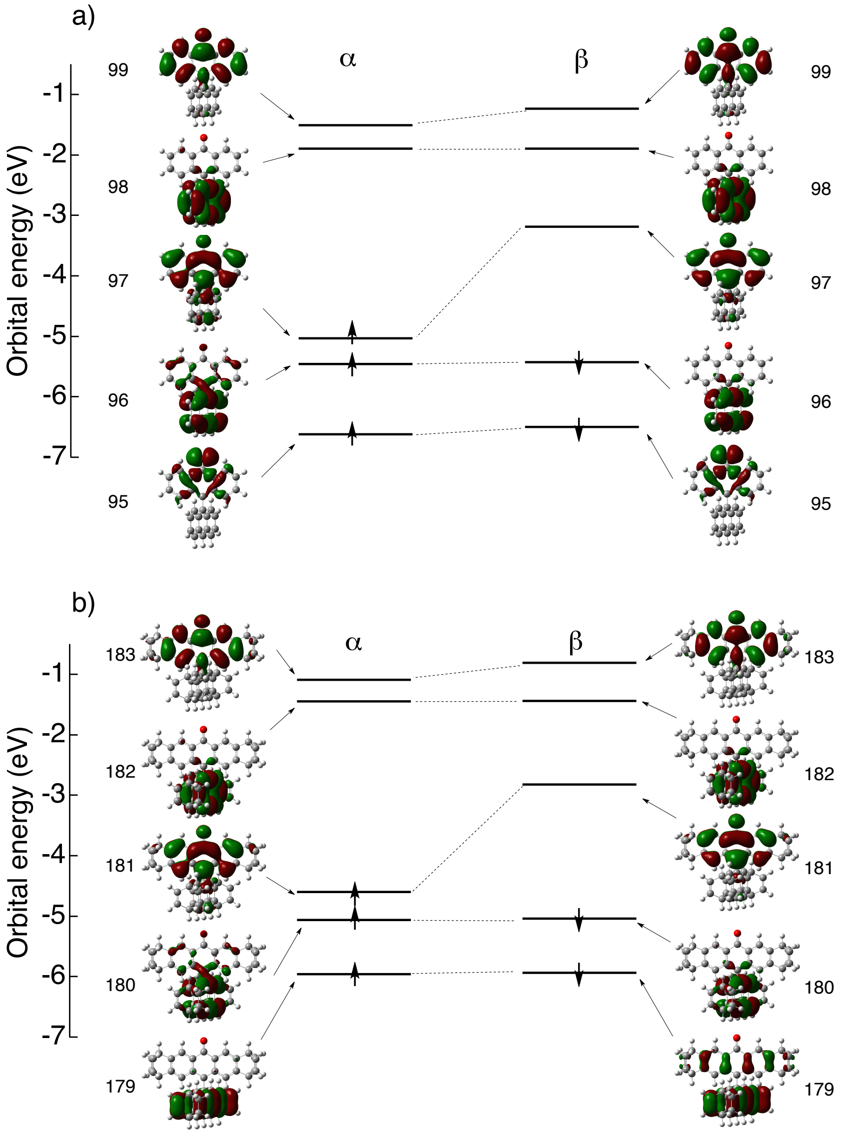

Fig. S7 Kohn–Sham orbitals of a) **1** and b) **2** computed at the B3LYP/6-31G(d) level.

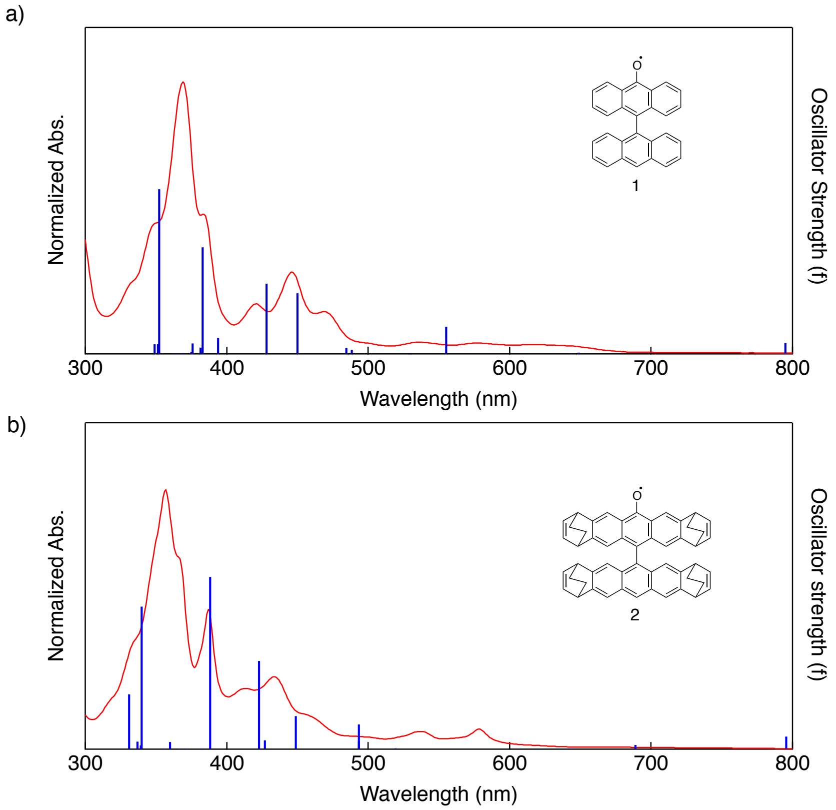

Fig. S8 UV-vis absorption spectra of a) **1** and b) **2** (red line) and theoretical peaks at the TD-B3LYP/6-31G(d) level (blue lines).

References:

[1] *a*) A. D. Backe, *J. Chem. Phys.,* 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[2] *a*) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys*., 1972, **56**, 2257; (*b*) P. C. Hariharan and J. A. Pople, *Theoret. Chimica. Acta,,* 1973, **28**, 213.

[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, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

4. Decay profiles of UV-vis absorption spectra of 1 and 2

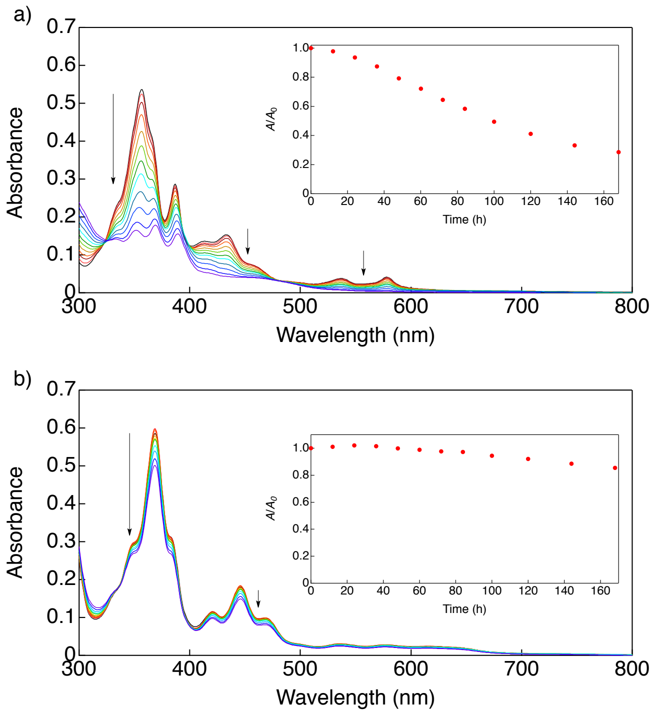

Fig. S9 Decay profiles of UV-vis absorption spectra of **1** (2.25×10^{-2} mM) and b) **2** (2.36×10^{-2} mM).

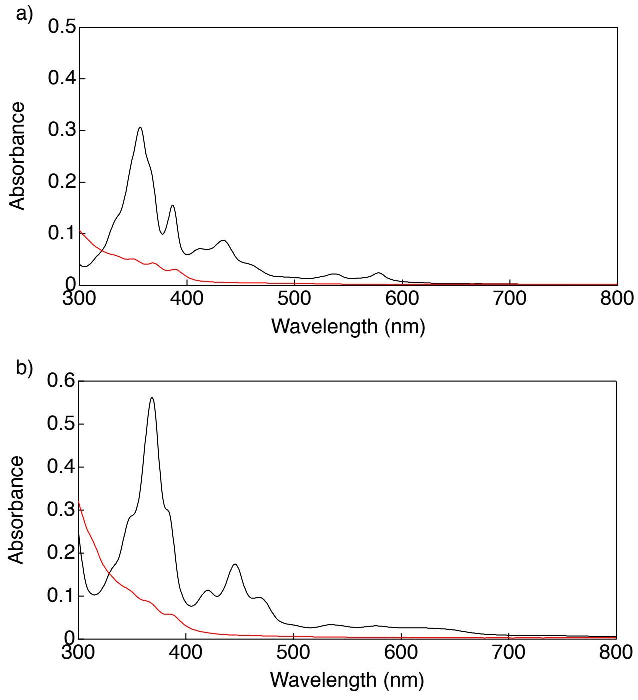

Fig. S10 UV-vis absorption spectral changes before (black) and after (red) decomposition. a) **1** (1.28×10^{-2} mM) and b) **2** (2.25×10^{-2} mM).

5. Redox potentials of 1 and 2.

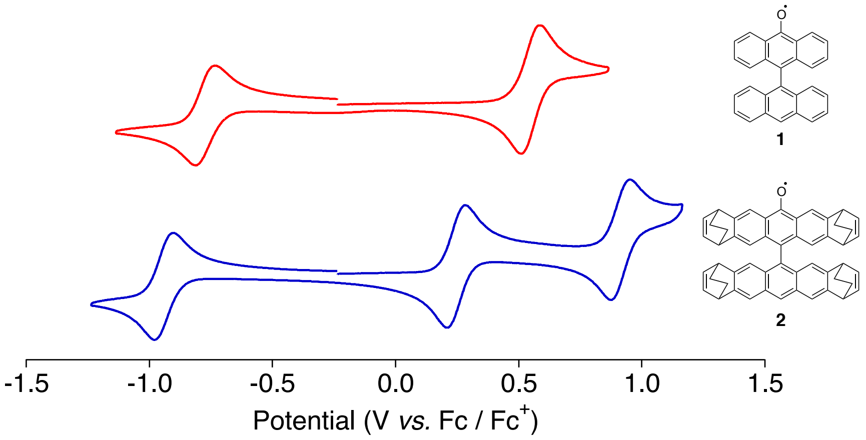

Fig. S11 Cyclic voltammograms of **1** (red) and **2** (blue) in dichloromethane with 0.1 M *n*Bu_4NPF_6, glassy carbon electrode, platinum counter electrode, and an Ag/$AgNO_3$ reference electrode. Scan rate = 100 mV/s.

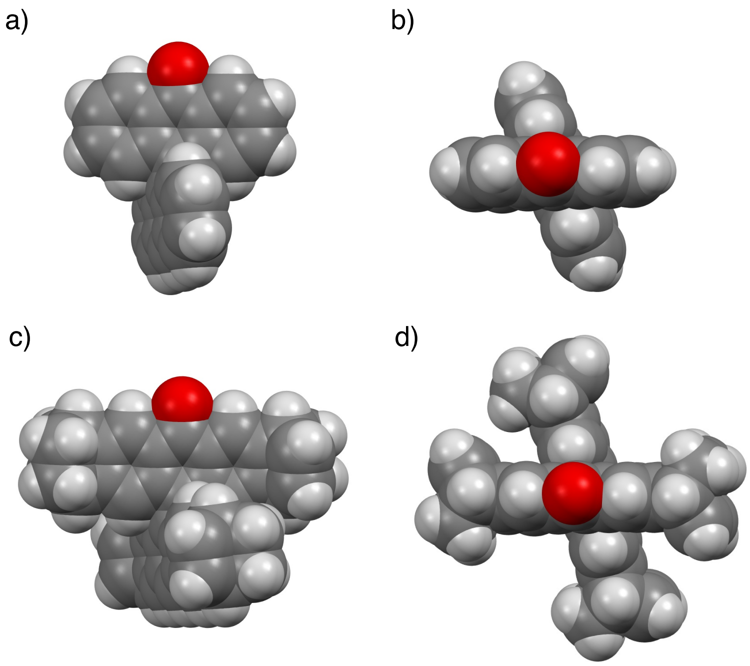

Fig. S12 Space-filling models of **1** (a: top view, b: side view) and **2** (c: top view, d: side view).

6. Thermal conversion of 2

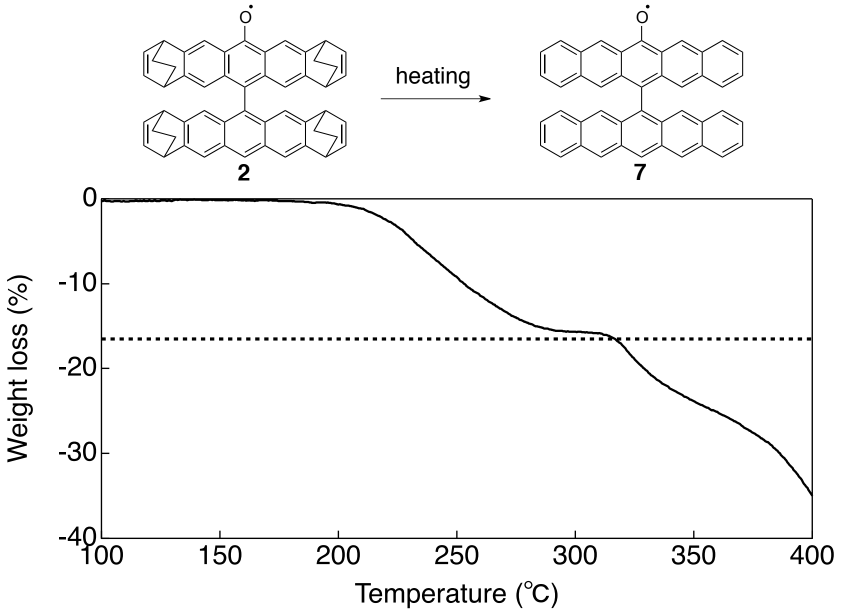

Fig. S13 Thermogravimetoric analysis of **2** (5 ºC/min).

Compound **2** (12 mg, 0.0176 mol) was suspended in ethylene glycol (3 ml). The mixture was bubbled with an argon gas for 20 min. The mixture was heated at 300 ºC for 5 min by microwave (Anton-Paar, Monowave 300). After cooling to room temperature, the precipitate was filtrated and washed with argon bubbled methanol. The product was dissolved in dry toluene and measured by APCI-MS spectrum.

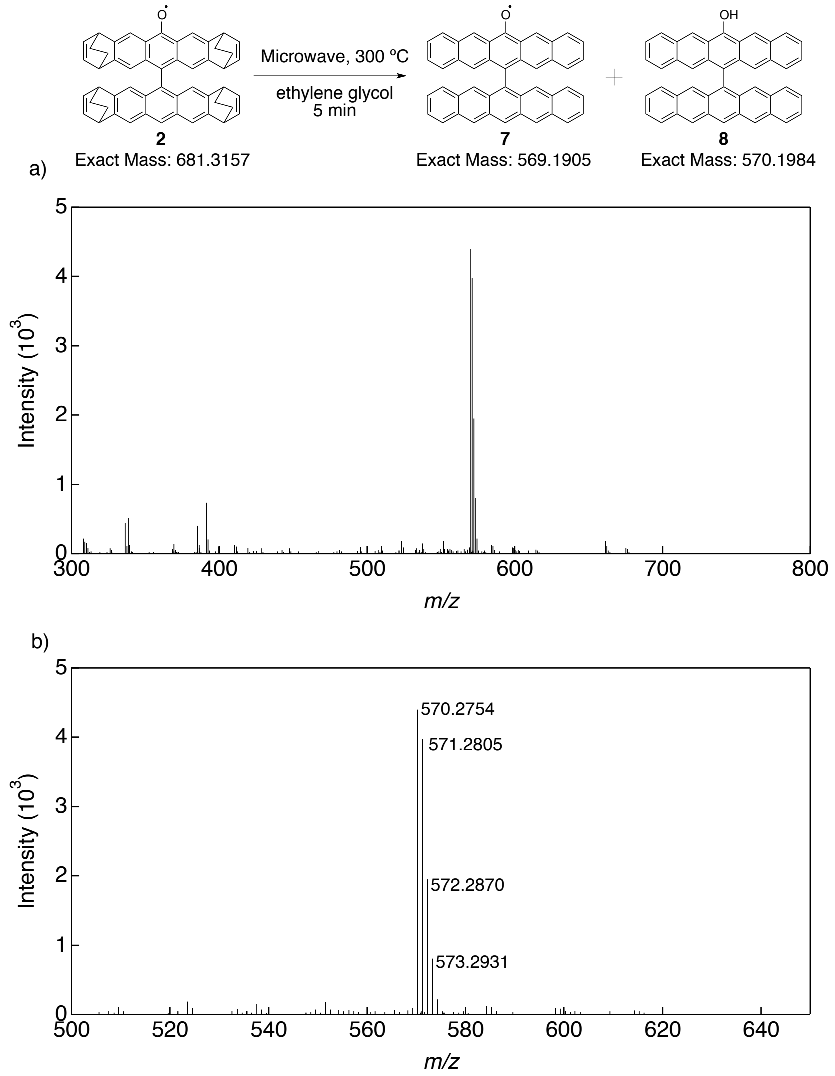

Fig. S14 APCI-MS spectra (positive) after thermal conversion of **2**.