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Electronic Supplementary Information

Oligo(maleic anhydride)s: a platform for unveiling the mechanism of clusteroluminescence of non-aromatic polymers

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Experimental section

Materials and Instrumentation: Maleic anhydride (MAh, 99%) and succinic anhydride (SAh, 99%) were purchased from Sigma-Aldrich. 2,4,4-Trimethyl-1-pentene (TMP, 98.0%) was purchased from TCI Co., Ltd. (Shanghai). Azobisisobutyronitrile (AIBN) was purchased from Xingang Chemical Co., Ltd. Butyl acetate (BA) was purchased from Aladdin Industrial Corporation. Tetrahydrofuran (THF), chloroform, acetone, and hexane were purchased from Guangzhou Chemical Reagent Factory. All these materials and solvents were purified according to the standard methods prior to use. Commercial PMMA were unfilled or pristine resins obtained from original manufacturers and plastics vendors. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500 NMR spectrometer using acetone-d_6 as solvents. The number average molecular weights (M_n) and weight average molecular weights (M_w), and polydispersity indices ($Đ = M_\mathrm{w}/M_\mathrm{n}$) of the oligomers and copolymers were evaluated by a Waters advanced polymers chromatography (APC) system with a PDA detector. THF was used as the solvent to dissolve the oligomers and copolymers (1 mg mL^{-1}). The solutions were filtered through 0.22 μm PTFE syringe-type filters before being injected into the APC system, and THF was used as the eluent at a flow rate of 0.5 mL min^{-1}. A set of linear polystyrene standards (Waters) covering the M_w range of 1×10^3–7×10^5 were utilized for M_w and $Đ$ calibration. Elemental analyses were carried out on a Vario EL-III elemental analyzer. UV-Vis absorption spectra were obtained on Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. The films were prepared on KW-4B spin coater from Institute of Microelectronics of Chinese Academy of Sciences.

Computational details: The geometry optimization was carried out at the level of density functional theory (DFT). The B3LYP functional was applied with 6-31G(d,p) basis set.[1] All these electronic structure calculations were performed with Gaussian 09 program package.[2] The distances and angles of PMP and OMAh4 were measured on

GaussView 5.0. The distances and angles of MAh and SAh were measured on Mercury 3.8.

Synthesis of OMAhs

To four 10 mL reaction tubes were added MAh (6 mmol, 0.588 g) and AIBN (47 mg) respectively. After degassed 3 times with dry nitrogen, 2 mL BA was injected into each of them. When the monomers and initiator were dissolved completely, the solutions were stirred at 70 °C under nitrogen for given time as shown in Table S1†. Then the reactions were cooled down to room temperature and 5 mL chloroform and appropriate amount of acetone were added until the solutions were clarified. The insoluble particles were filtered through cotton. The filtrates were precipitated in chloroform/hexane (50/100 mL) twice. The precipitates were collected by centrifugum (7000 r/min, 2 min) and finally dried at 40 °C under vacuum for 12 hours. OMAhs were obtained in 1.5, 2.6, 4.7, 7.9% yields as Pale brown powders, respectively. M_w: 1060, 1100, 1180, 1200. $Đ$: 1.02, 1.03, 1.06, 1.07. ^{1}H NMR (500 MHz, Acetone-d_6), δ (ppm): 4.22. ^{13}C NMR (125 MHz, Acetone-d_6), δ (ppm): 48.88, 172.32.

Synthesis of PMPs

To four 10 mL reaction tubes were added MAh (6 mmol, 0.588 g) and AIBN (47 mg) respectively. After degassed 3 times with dry nitrogen, 2 mL BA was injected into each of them. Then TMP (6 mmol, 0.94 mL) was injected into the first tube. When solids were dissolved completely, this solution was allowed to polymerize at 70 °C under nitrogen for 4 hours. At the same time, TMP (6 mmol, 0.94 mL) was added into the other tubes after MAh homopolymerized for 1, 2, and 3 hours, respectively and their total reaction time were controlled to be 4 hours. Afterwards, the polymerizations were cooled down to room temperature. The products were precipitated in chloroform/hexane (50/100 mL) three times. The precipitates were collected by centrifugation (7000 r/min, 2 min) and finally dried at 40 °C under vacuum for 12 hours. PMP, PMP1, PMP2, PMP3 with M_w of 39900, 42200, 40800, 43000 and $Đ$ of 1.41, 1.36, 1.34, 1.31 were obtained in 61, 27, 30, 25% yields as white powder, pale brown powders, respectively.

PMP: ^{1}H NMR (500 MHz, Acetone-d_6), δ (ppm): 1.06, 1.13, 1.20–1.80, 1.80–2.66, 3.20–4.03. ^{13}C NMR (125 MHz, Acetone-d_6), δ (ppm): 24.64, 32.51, 33.02, 41.67, 42.99, 49.38, 51.97, 58.09, 172.58, 175.10.

PMP1: ^{1}H NMR (500 MHz, Acetone-d_6), δ (ppm): 1.06, 1.13, 1.20–1.80, 1.80–3.17, 3.28–4.04, 4.05–4.90.

PMP2: ^{1}H NMR (500 MHz, Acetone-d_6), δ (ppm): 1.06, 1.13, 1.20–1.80, 1.80–3.26, 3.28–4.04, 4.05–4.90.

PMP3: ^{1}H NMR (500 MHz, Acetone-d_6), δ (ppm): 1.06, 1.13, 1.20–1.80, 1.80–2.93, 3.26–4.04, 4.05–5.00.

Recrystallization and distillation

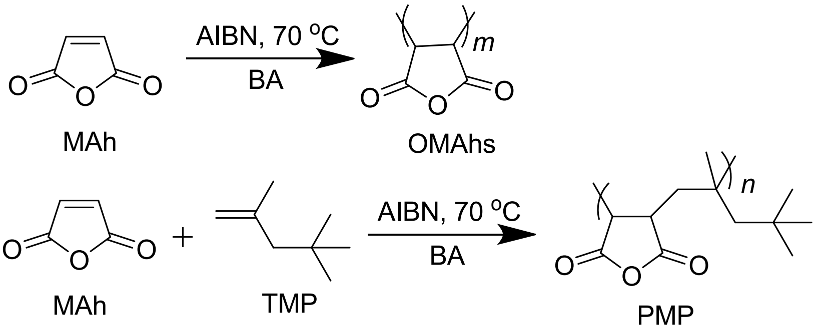
Saturated solution of maleic anhydride (MAh) was prepared in chloroform/hexane at 65 ^{o}C and recrystallized at 0 ^{o}C. Saturated solution of SAh was prepared in chloroform at 65 ^{o}C and recrystallized at room temperature. Saturated solution of AIBN was prepared in absolute alcohol at 80 ^{o}C and recrystallized at room temperature. 2,4,4-Trimethyl-1-pentene (TMP) was distilled at 50 ^{o}C under vacuum (vacuum degree: 0.083 MPa). *n*-Butyl acetate (BA) was treated by anhydrous $NaCO_3$, $CaCl_2$ and $MgSO_4$ prior to distill and then distilled at 150 ^{o}C. THF was distilled from sodium benzophenone ketyl under nitrogen. Hexane was treated by 95 wt% H_2SO_4 prior to distill and then distilled at 100 ^{o}C.

Preparation of the aggregates of OMAh4

Stock THF solution of OMAh4 with a concentration of 5×10^{-3} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, hexane was added dropwise under vigorous stirring to furnish 2×10^{-4} M solutions with different hexane fractions (0–90 vol%). Because OMAh4 is soluble in THF but insoluble in hexane, the oligomer chains must have aggregated into nanoaggregates when large amount hexane fractions are added. The PL spectra measurements of the resultant solutions were then performed immediately.

Preparation of doped PMMA films

The OMAh doped film was given here as an example. 2 mL PMMA THF solution with concentration of 50 mg/mL was first prepared. 7.5 mg OMAh was added into 0.1 mL PMMA solution and mixed thoroughly. 60 wt% film was obtained after 10 μL mixtures was dropped on the quartz plates (1 cm×1 cm) and then spinned on spin coater. Other films were obtained by the same way.



Scheme S1. Synthetic routes to OMAhs and PMP.

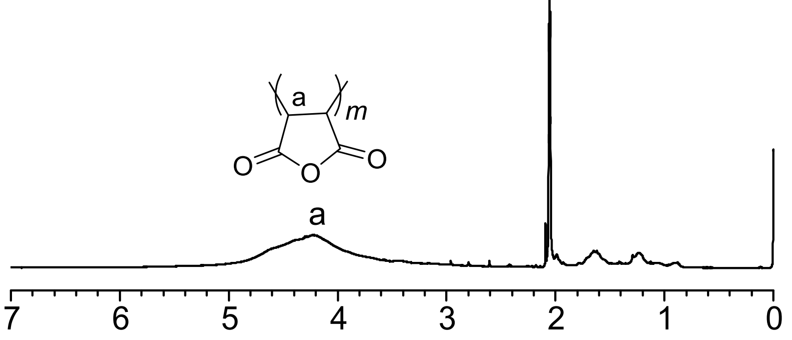


Fig. S1 ^{1}H NMR spectra of OMAh4 in acetone-d_6. The solvent peak is marked with asterisk.

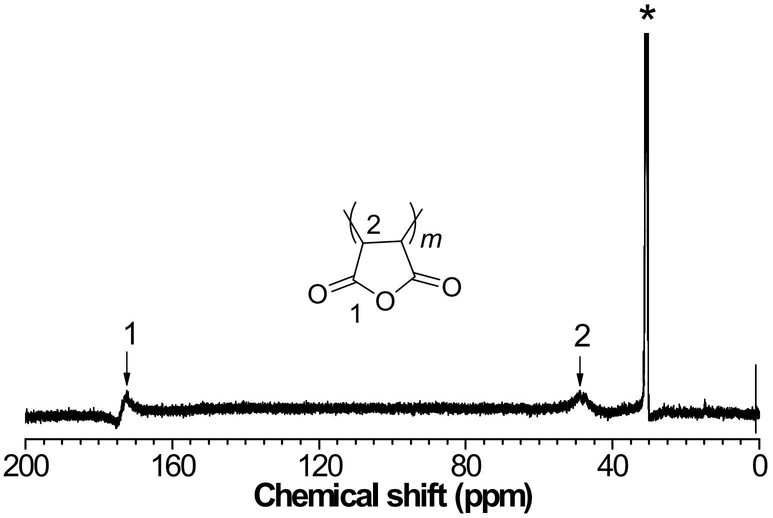


Fig. S2 ^{13}C NMR spectra of OMAh4 in acetone-d_6. The solvent peak is marked with asterisk.

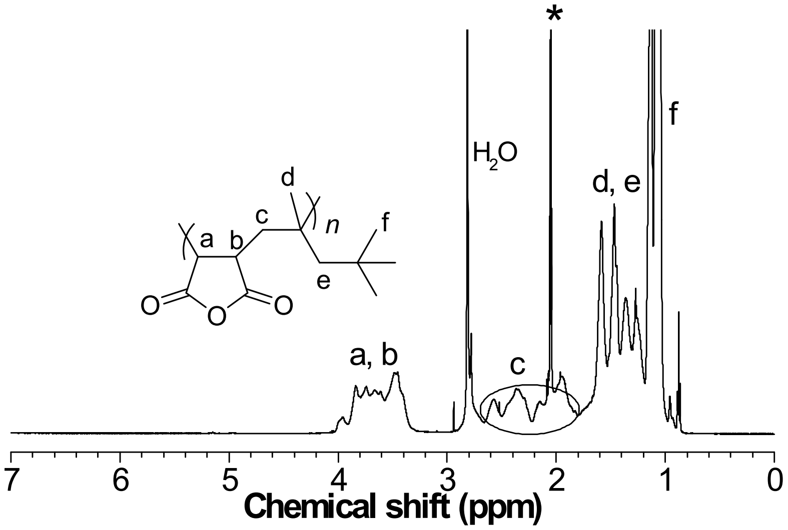


Fig. S3 ^{1}H NMR spectra of PMP in acetone-d_6. The solvent peak is marked with asterisk.

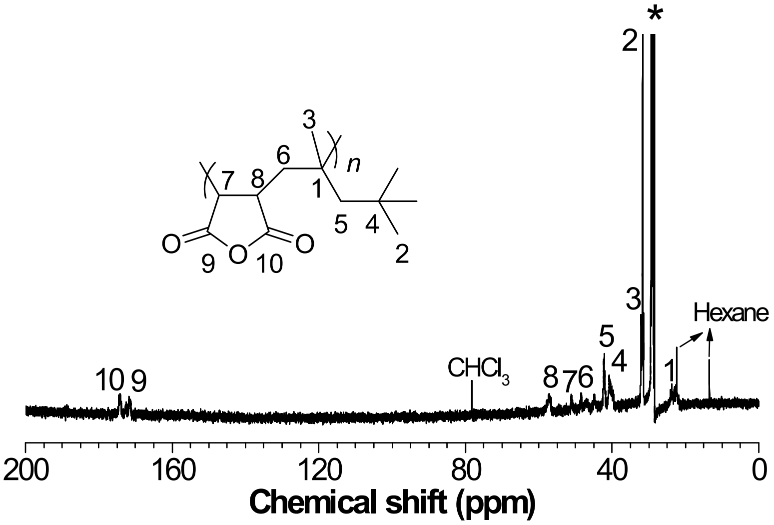


Fig. S4 ^{13}C NMR spectra of PMP in acetone-d_6. The solvent peak is marked with asterisk.

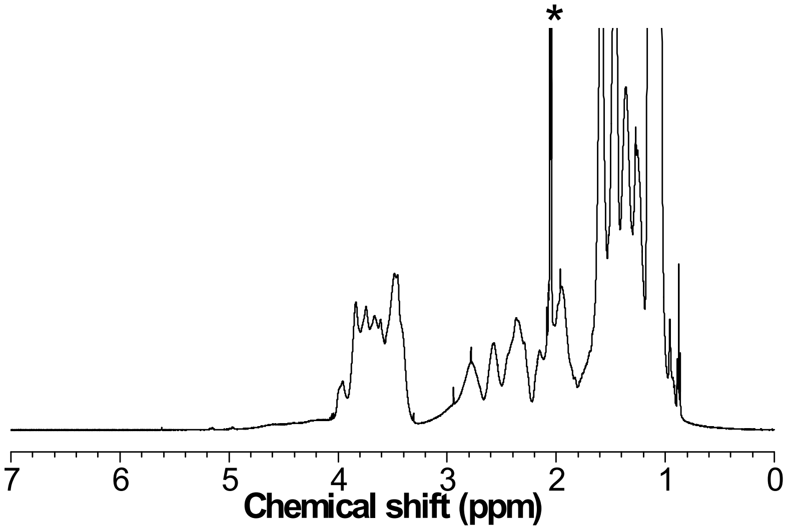


Fig. S5 ^{1}H NMR spectra of PMP1 in acetone-d_6. The solvent peak is marked with asterisk.

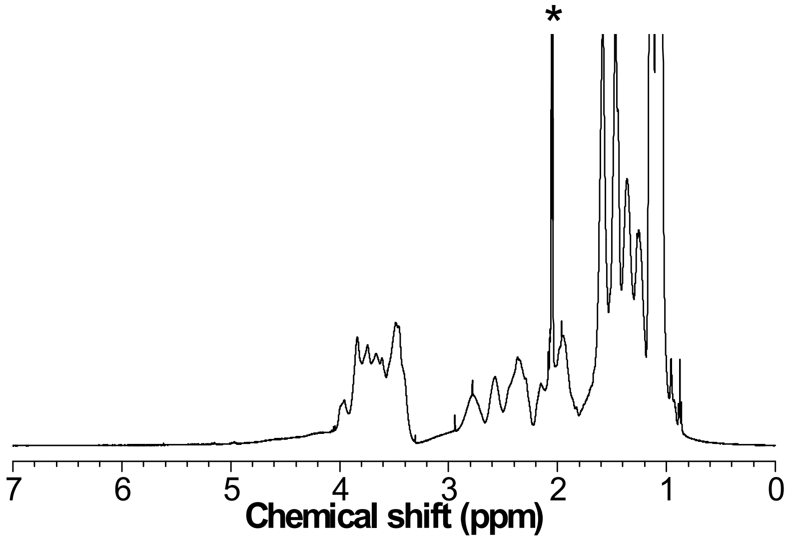


Fig. S6 ^{1}H NMR spectra of PMP2 in acetone-d_6. The solvent peak is marked with asterisk.

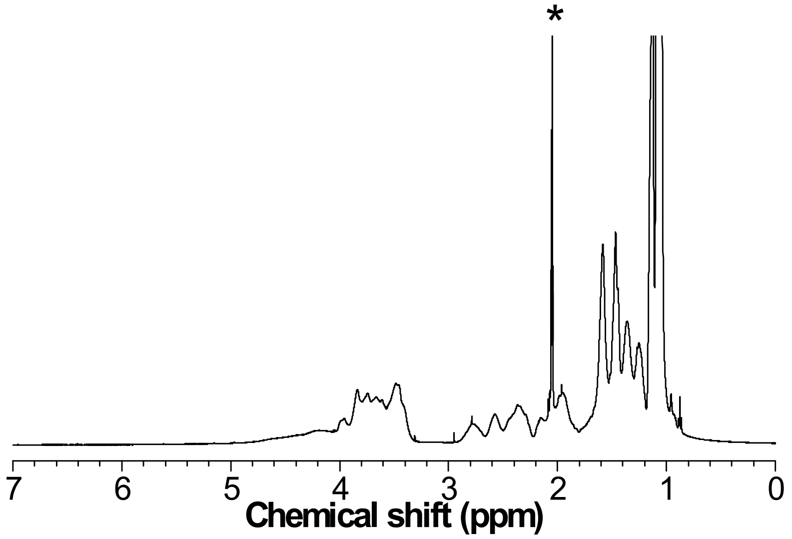


Fig. S7 ^{1}H NMR spectra of PMP3 in acetone-d_6. The solvent peak is marked with asterisk.

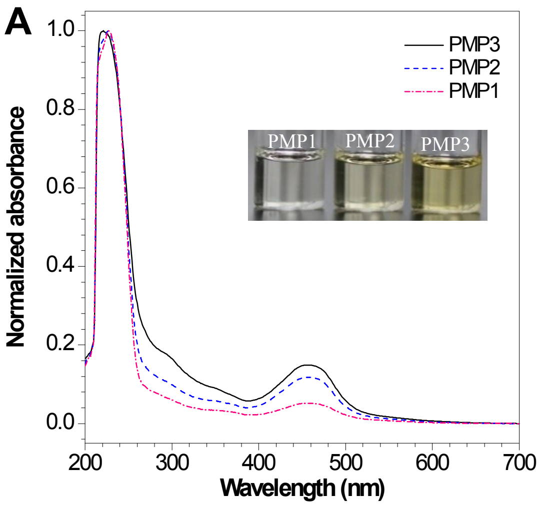


Figure S8. UV-Vis (A) and PL (B) spectra of PMP1, PMP2 and PMP3 in THF. Concentration: 2 mg/mL, excitation wavelength: 365 nm.

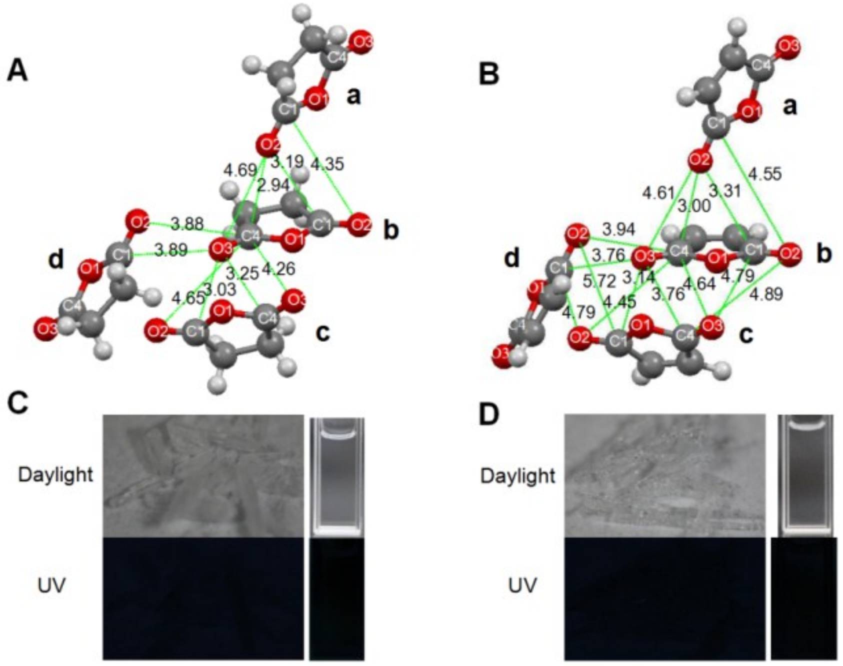


Figure S9. Crystal structures of SAh (A) and MAh (B), and photographs of SAh (C) and MAh (D) THF solutions and crystals under daylight and UV irradiation. Concentration: 0.01 M, excitation wavelength: 365 nm.

Table S1 Polymerization results of OMAhs[a]

t (h)[b]	*oligomer*	M_w[c]	*Đ*[c]	yield (%)[d]
1	OMAh1	1200	1.07	1.5
2	OMAh2	1180	1.06	2.6
3	OMAh3	1100	1.03	4.7
4	OMAh4	1060	1.02	7.9

[a] Initiated by AIBN (concentration: 0.14 M) in *n*-Butyl acetate (BA) at 70 °C. [b] reaction time. [c] Determined by advanced polymer chromatography (APC) in THF on the basis of a linear polystyrene calibration. Polydispersity indices (*Đ*) = M_w/M_n. [d] isolated yield.

Table S2. Elemental analysis of copolymers

Copolymer	C(%)	H(%)	N(%)	O(%)	[MAh]:[TMP]
PMP	68.70	9.29	0.04	21.97	0.94:1
PMP1	67.81	9.23	0.11	22.85	1.02:1
PMP2	67.09	8.83	0.19	23.89	1.11:1
PMP3	64.76	8.15	0.34	26.75	1.41:1

Table S3 Conformational parameters of optimized model of OMAh4[a]

O---C	*d* (Å)	O---C=O	*θ* (˚)
O_{74}---C_{77}	3.11	O_{74}---C_{77}=O_{81}	97.10
O_{81}---C_{70}	3.12	O_{81}---C_{70}=O_{74}	96.66
O_{73}---C_{52}	2.96	O_{73}---C_{52}=O_{55}	89.38
O_{55}---C_{68}	2.89	O_{55}---C_{68}=O_{73}	92.89
O_{54}---C_{43}	3.13	O_{54}---C_{43}=O_{47}	101.63
O_{47}---C_{50}	3.18	O_{47}---C_{50}=O_{54}	98.85
O_{46}---C_{25}	2.84	O_{46}---C_{25}=O_{28}	95.37
O_{28}---C_{41}	3.14	O_{28}---C_{41}=O_{46}	81.10
O_{27}---C_{16}	3.11	O_{27}---C_{16}=O_{19}	97.21
O_{19}---C_{23}	3.12	O_{19}---C_{23}=O_{27}	96.80

[a] shown in Fig. 3A and 3C

Table S4 Conformational parameters of optimized model of PMP[a]

O---C	*d* (Å)	O---C=O	θ (˚)
O_{13}---C_{18}	5.31	O_{13}---C_{18}=O_{23}	62.34
O_{23}---C_{11}	4.90	O_{23}---C_{11}=O_{13}	81.44
O_{27}---C_{31}	5.37	O_{27}---C_{31}=O_{36}	80.52
O_{36}---C_{21}	5.03	O_{36}---C_{21}=O_{27}	96.77
O_{49}---C_{34}	5.00	O_{49}---C_{34}=O_{40}	76.99
O_{40}---C_{44}	5.13	O_{40}---C_{44}=O_{49}	70.74
O_{62}---C_{47}	5.07	O_{62}---C_{47}=O_{53}	82.75
O_{53}---C_{57}	5.27	O_{53}---C_{57}=O_{62}	73.42
O_{75}---C_{60}	5.10	O_{75}---C_{60}=O_{66}	81.85
O_{66}---C_{70}	5.30	O_{66}---C_{70}=O_{75}	80.05
O_{79}---C_{83}	5.30	O_{79}---C_{83}=O_{88}	70.60
O_{88}---C_{73}	5.07	O_{88}---C_{73}=O_{79}	81.62
O_{101}---C_{86}	5.07	O_{101}---C_{86}=O_{92}	84.51
O_{92}---C_{96}	5.26	O_{92}---C_{96}=O_{101}	75.73
O_{105}---C_{109}	5.13	O_{105}---C_{109}=O_{114}	69.02
O_{114}---C_{99}	4.96	O_{114}---C_{99}=O_{105}	76.65
O_{127}---C_{112}	5.22	O_{127}---C_{112}=O_{118}	89.62

[a] shown in Fig. 3B

Table S5 Conformational parameters of MAh extracted from the crystal[a] (CCDC number: 1212552)

O---C	*d* (Å)	O---C=O	θ (˚)
(a)O_2---C_1(b)	3.31	(a)O_2---C_1=O_2(b)	115.10
(b)O_2---C_1(a)	4.55	(b)O_2---C_1=O_2(a)	53.33
(a)O_2---C_4(b)	3.00	(a)O_2---C_4=O_3(b)	101.05
(b)O_3---C_1(a)	4.61	(b)O_3---C_1=O_2(a)	4.54
(b)O_3---C_4(c)	3.76	(b)O_3---C_4=O_3(c)	123.07
(c)O_3---C_4(b)	4.64	(c)O_3---C_4=O_3(b)	77.24
(b)O_3---C_1(c)	3.14	(b)O_3---C_1=O_2(c)	95.28
(c)O_2---C_4(b)	4.45	(c)O_2---C_4=O_3(b)	29.22
(b)O_2---C_4(c)	4.89	(b)O_2---C_4=O_3(c)	80.53
(c)O_3---C_1(b)	4.79	(c)O_3---C_1=O_2(b)	85.34
(d)O_2---C_4(b)	3.94	(d)O_2---C_4=O_3(b)	64.04
(b)O_3---C_1(d)	3.76	(b)O_3---C_1=O_2(d)	72.50
(d)O_2---C_1(c)	5.72	(d)O_2---C_1=O_2(c)	69.08
(c)O_2---C_1(d)	4.79	(c)O_2---C_1=O_2(d)	115.77

[a] shown in Fig. S9B

Table S6 Conformational parameters of SAh extracted from the crystal[a] (CCDC number: 171946)

O---C	d (Å)	O---C=O	θ (°)
(a)O_2---C_1(b)	3.19	(a)O_2---C_1=O_2(b)	118.19
(b)O_2---C_1(a)	4.35	(b)O_2---C_1=O_2(a)	60.29
(a)O_2---C_4(b)	2.94	(a)O_2---C_4=O_3(b)	107.47
(b)O_3---C_1(a)	4.69	(b)O_3---C_1=O_2(a)	2.52
(b)O_3---C_4(c)	3.25	(b)O_3---C_4=O_3(c)	114.28
(c)O_3---C_4(b)	4.26	(c)O_3---C_4=O_3(b)	64.49
(b)O_3---C_1(c)	3.03	(b)O_3---C_1=O_2(c)	104.52
(c)O_2---C_4(b)	4.65	(c)O_2---C_4=O_3(b)	17.90
(d)O_2---C_4(b)	3.88	(d)O_2---C_4=O_3(b)	71.85
(b)O_3---C_1(d)	3.89	(b)O_3---C_1=O_2(d)	71.45

[a] shown in Fig. S9A

References:

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

(2) 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.