Electronic Supplementary Information

Synthesis of Polyacenequinones via Crossed Aldol Condensation in Pressurized Hot Water in the Absence of Added Catalysts

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Instrumentations

GC-MS analyses, Gas Chromatograph Mass Spectrometric Analysis: This was carried out on a Shimadzu GCMS-QP2010 spectrometer. The solid sample was dissolved in *o*-dichlorobenzene and a 0.5 mL aliquot was injected with a split ratio of 100 with the flow rate of helium carrier gas of 28 cm/s. After being kept at 60 ^{o}C for 4 min, it was heated up to 280 ^{o}C with a rate of 20 ^{o}C/min and kept there for 30 min.

Melting point measurement: Thermograms were recorded on a Bruker AXS TG-DTA2020SA TG-DTA analyzer with a rate of 20 ^{o}C/min at 20~450 ^{o}C.

NMR spectra: Spectra of a very dilute saturated solution of the solid sample in chloroform-d with TMS as an internal standard were obtained on a BRUKER AXS NMR-Avance-400 spectrometer at 400 MHz.

FT-IR spectra: The solid sample in KBr discs was measured on a Shimadzu FTIR-8400S spectrometer.

Analyses of the filtrate

The combined filtrate was analyzed by means of a Shimadzu GC-2010 gas chromatograph analyzer (GC/FID). A 1 mL aliquot was injected with a split ratio of 100 with the flow rate of carrier gas helium of 20 cm/s. After being kept at 60 ^{o}C for 4 min, the column was heated up to 280 ^{o}C with a rate of 20 ^{o}C/min and kept there for 30 min. The amount of the unreacted starting materials was determined accurately by using added 1-hexanol as an internal standard and calibration curves obtained independently for the pure starting materials.

6,13-pentacenequinone

a) An endothermic peak corresponding to melting was observed at 394 ^{o}C in the DTA analysis in good agreement with the reported melting point.[21]

b) The parent and base peak at m/z = 308 agreed nicely with the molecular weight of the quinone. A relatively strong m/z = 309 peak was characteristic of quinones that readily pick up a hydrogen atom in the electron ionization mass spectrometry.

c) FT-IR spectra of a KBr disc sample showed peaks characteristic of carbonyl absorptions at 1690-1660 cm^{-1}.

d) ^{1}H-NMR showed a singlet at d 8.97 due to four protons at 5-, 7-, 12- and 14-positions on the inner benzene

rings, and an A_2X_2 pattern characteristic of a symmetrically *o*-disubstituted benzene at *d* 8.15 and 7.73 for 1-, 4-, 8, 11-protons, and 2-, 3-, 9- and 10-protons, respectively.

7,16-heptacenequinone

The parent and base peak at *m/z* = 408 agreed nicely with the molecular weight of the quinone. Strong FT-IR absorptions at IR 1682, 1670, 1228cm^{-1} agreed nicely with those of the heptacenequinone in the literature (ref. 2 1 and Beilstein Ref. 4-07-00-02689).

5,12-naphthacenequinone

Their mass, ^{1}H NMR and FT-IR spectra agreed nicely with those of the naphthacenequinone in the literature.[22]

2. Tables S1~S5. Numerical data supporting Fig. 2~6 for the formation of 6,13-pentacenequinone under variou s conditions 1

Table S1 Yield of 6,13-pentacenequinone and decrease of the starting materials for a series of reactions in 3.574-g water (except zero water) at 250 ^{o}C for 20 min

Molar ratio of water to phthalaldehyde	6,13-pentacene-quinone /g (mol %)	1,4-cyclohexane-dione /g (mol %)	phthalaldehyde /g (mol %)
0 (ave. of 2 runs)	0.001 (0.9)	(98.5)	0.880 (79.5)
50	0.126 (20.6)	0.223 (88.4)	0.533 (48.1)
100	0.0922 (30.3)	0.111 (39.2)	0.266 (24.0)
150	0.0826 (40.7)	0.0742 (27.0)	0.178 (16.8)
200	0.0783 (50.5)	0.0557 (22.1)	0.133 (19.3)
250	0.0629 (51.9)	0.0442 (17.3)	0.106 (18.2)
300	0.0521 (51.1)	0.0371 (16.1)	0.0888 (8.2)
400 (3 runs)	0.0420 (54.6±2.2)	0.0048 (17.2±2.2)	0.0145 (21.8±4.3)

Table S2 Temporal development of the amounts of 6,13-pentacene-quinone and starting materials in 100-fold excess water at 250 °C

reaction time /min	6,13-pentacene-quinine /g (mol %)	1,4-cyclohexane-dione /g (mol %)	phthalaldehyde /g (mol %)
1	0.00180 (0.59)	0.0774 (68.8)	0.180 (67.3)
4	0.0391 (12.66)	0.0549 (48.9)	0.118 (43.8)
7	0.0584 (19.18)	0.0504 (45.6)	0.0984 (37.0)
10	0.0703 (23.30)	0.0517 (47.2)	0.0930 (35.0)
20	0.0922 (30.29)	0.0434 (39.2)	0.0643 (24.0)
30	0.0928 (30.25)	0.0384 (33.2)	0.0476 (17.8)

Table S3 Temporal development of the amounts of 6,13-pentacenequinone and starting materials in 400-fold excess water at 250 °C

reaction time /min	6,13-pentacene-quinone /g (mol %)	1,4-cyclohexanedione /g (mol %)	phthalaldehyde /g (mol%)
3 (4 runs)	0.0065 (8.5±2.0)	0.0061 (21.8±15.0)	0.0198 (29.7±14.4)
5 (4 runs)	0.0146 (19.1±3.0)	0.0060 (21.6±13.3)	0.0186 (28.0±13.0)
7 (4 runs)	0.0209 (27.2±2.5)	0.0090 (32.4±10.0)	0.0143 (21.5±9.3)
10	0.0309 (40.3)	0.0056 (20.1)	0.0162 (24.4)
20(3 runs)	0.0418 (54.6±2.2)	0.0048 (17.2±2.2)	0.0145 (21.8±4.3)
30	0.0505 (65.9)	0.0034 (12.1)	0.0077 (11.5)
60	0.0590 (76.9)	0.0034 (12.2)	0.0027 (4.1)

Table S4 Effect of temperature on the yield of 6,13-pentacenequinone /g (mol %)

reaction time /min	temperature				
	230 °C	250 °C	300 °C	370 °C	400 °C
3 (4 runs)	0.0021 (2.7)	0.0065 (8.5±2.0)	0.0133 (17.3)	0.0158 (20.6)	0.0187 (24.4)
5 (4 runs)	0.0083 (10.8)	0.0147 (19.1±3.0)	0.0244 (31.9)	0.0145 (19.0)	0.0083 (10.8)
7 (4 runs)	0.0129 (16.8)	0.0209 (27.2±2.5)	0.0292 (38.1)	0.0231 (30.1)	0.0193 (25.1)
10	0.193 (25.2)	0.0309 (40.3)	0.0289 (37.7)	0.0206 (26.9)	0.0144 (18.8)
20 (3 runs)	0.0320 (41.8)	0.0419 (54.6±2.2)	0.0424 (55.2)	0.0257 (33.6)	0.0165 (21.5)
30	0.0387 (50.5)	0.0506 (65.9)	0.0467 (60.9)	0.0344 (44.9)	0.0178 (23.3)

Table S5 Results of the molar yield of 6,13-pentacenequinone /g (mol %).

tempera-ture/ ^{o}C	reaction time /min	pH 3	pH 4	pH 7	pH 10
230	3	0 (0)	0.00052 (0.68)	0.0021 (2.7)	0.0012 (1.6)
	5	0.0025 (3.24)	0.0077 (10.1)	0.0083 (10.8)	0.0077 (10.1)
	7	0.0054 (7.03)	0.0086 (11.2)	0.0129 (16.8)	0.0094 (12.3)
250	3	0.0017 (2.25)	0.0054 (6.89)	0.0065 (8.49)	0.0085 (11.0)
	5	0.0055 (7.18)	0.012 (14.8)	0.015 (19.1)	0.016 (20.9)
	7	0.0094 (12.3)	0.017 (22.6)	0.021 (27.2)	0.022 (28.6)
370	3	0.0079 (10.3)	0.0088 (11.7)	0.016 (20.5)	0.017 (22.3)
	5	0.0137 (18.2)	0.0139 (18.1)	0.0145 (19.0)	0.0270 (34.8)
	7	0.0162 (20.8)	0.0192 (25.1)	0.0231 (30.1)	0.0426 (55.0)

3. The equations necessary for calculating real pH values under reaction conditions as shown in Table 1.

For reaction equilibria,

$H_2O = H^+ + OH^-$

$$K_{H_2O} = \frac{[H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-}}{a_{H_2O}} \qquad (5\text{-}1)$$

$HCl(aq) = H^+ + Cl^-$

$$K_{HCl} = \frac{[H^+]\gamma_{H^+}[Cl^-]\gamma_{Cl^-}}{[HCl(aq)]} \qquad (5\text{-}2)$$

$NaOH(aq) = Na^+ + OH^-$

$$K_{NaOH} = \frac{[Na^+]\gamma_{Na^+}[OH^-]\gamma_{OH^-}}{[NaOH(aq)]} \quad (5\text{-}3)$$

For ions balance,

$[Cl]_{total} = [HCl(aq)] + [Cl^-]$ (5-4)

$[Na]_{total} = [NaOH(aq)] + [Na^+]$ (5-5)

For charge balance,

$[H^+] + [Na^+] = [OH^-] + [Cl^-]$ (5-6)