Supporting Information

Unidirectional growth of organic single crystals of naphthalene, anthracene and pyrene by isothermal expansion of supercritical CO_2

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1. Measurement of depressurized CO₂.

Depressurized CO_2 was measured through pneumatic trough as described in Fig S2. The outlet of crystallizer vent was connected to the inlet shown by "→". A flat container of 5 L (1) was taken and filled with 2.5 L water. A graduated cylinder (2) (diameter 20 cm, height 10 cm) was completely filled with water and placed inverted into 1. Incoming CO_2 from crystallizer vessel as shown through arrow (→) was passed through the tube (3) that is inserted under water into 2 as shown in Fig S2. Collected CO_2 (4) was measured with respect to time as per the pre-calibrated water level.

2. Determination of rate of crystallization

The rate of crystallization was calculated as described below.

Volume of crystallizer Vc = 100 mL

Working Pressure P_w = 120 bar = 118.43 atm

Depressurization pressure P_d = 1 atm

Volume of CO_2 in 1 atm, V_{atm} was obtained from eq 1.

Depressurization rate (mL/min) = R_d

Time required for complete depressurization (t) in sec was obtained from eq 2.

Crystal length measured in mm = l

$$l_c = \frac{l}{1000}$$
Crystal length in meter

Growth rate R in m.s-1 was obtained from eq 3.

$$V_{atm} = \frac{P_w V_c}{P_d} \quad (1)$$

$$t = \frac{V_{atm}}{R_d} x60 \quad (2)$$

$$R = \frac{l_c}{t} \qquad (3)$$

For example, Growth rate of anthracene ((Table 2, in present work) in m.s^{-1}

$$R_{anthracene} = \frac{l_c}{t} = \frac{l_c R_d}{V_{atm}.60} = \frac{l_c R_d P_d}{P_w V_c.60000} = \frac{2x10x1}{118.43x100x60000} = 2.8 \times 10^{-8}$$

Table S1: Recycle test of anthracene crystallization.[a]

Recycle Nos.	W_0 (g)	W_c (g)	W_p (g)	W_a (g)	% Yield [(W_c/W_0) x 100]
1	2	1.35	0.52	1.48	67.09
2	2	1.30	0.54	1.46	65.0
3	2	1.33	0.43	--	66.5

a) CO_2 120 bar; temperature 45 °C; depressurization 10 mLper min. W_0 weight taken; W_c weight of crystals obtained (g) W_p weight of powder after cycle.
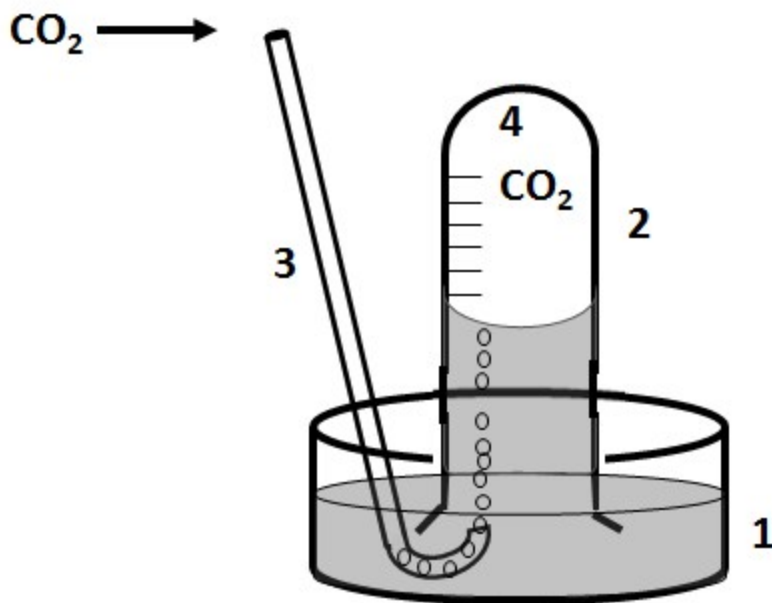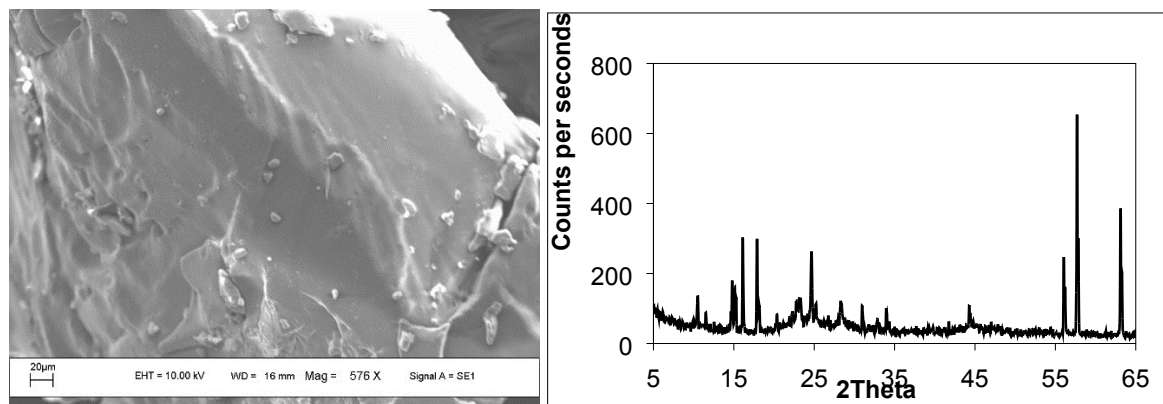
Fig S1. Pneumatic trough gas collection for measurement of depressurized CO_2 gas collected to crystallizer vent.

(a)   (b)
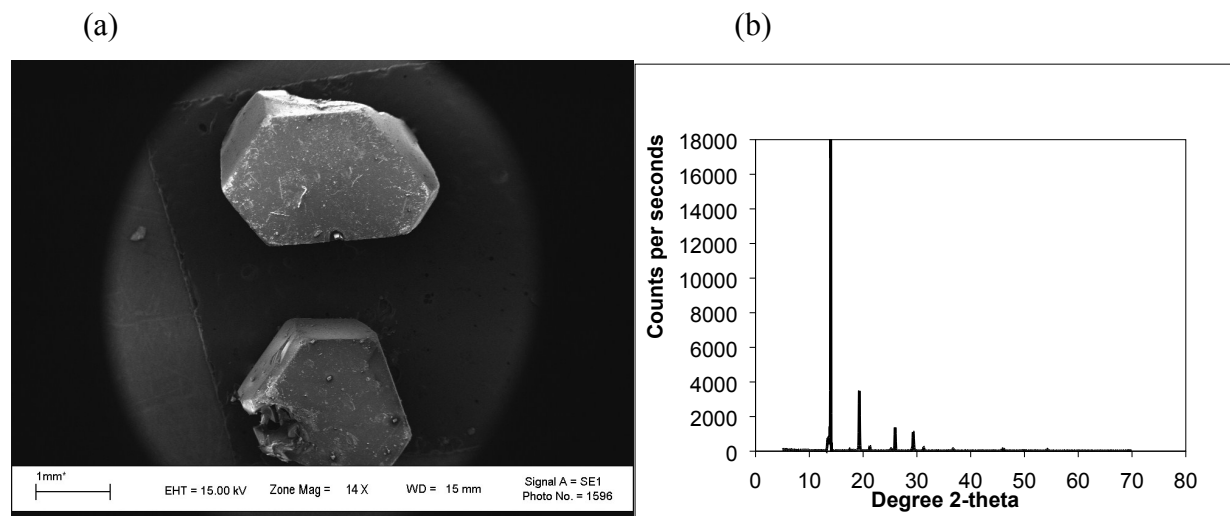
Fig. S2. a) SEM Image, b) XRD of naphthalene crystal. CO_2 120 bar, temp. 45°C, depressurization 10 mL per min, FWHM for 2θ 13.96° [001] 0.0856.

(a)   (b)

Fig. S3. a) SEM Image, b) XRD of anthracene crystal. CO_2 120 bar, temp. 45°C, depressurization rate 50 mL per min.