

Electronic Supporting Information

# Functional isocoumarin-containing polymers synthesized by rhodium-catalyzed oxidative polycoupling of aryl diacid and internal diyne

Ting Han,<sup>ab</sup> Haiqin Deng,<sup>ab</sup> Chris Y. Y. Yu,<sup>ab</sup> Chen Gui,<sup>ab</sup> Zhegang Song,<sup>ab</sup> Ryan T.

K. Kowk,<sup>ab</sup> Jacky W. Y. Lam,<sup>\*ab</sup> and Ben Zhong Tang<sup>\*abc</sup>

<sup>a</sup> HKUST-Shenzhen Research Institute, No. 9 Yuexing 1st RD, South Area, Hi-tech Park, Nanshan, Shenzhen 518057, China

<sup>b</sup> Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, Institute for Advanced Study, Institute of Molecular Functional Materials, Division of Biomedical Engineering, Division of Life Science and State Key Laboratory of Molecular Neuroscience, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong

<sup>c</sup> Guangdong Innovative Research Team, SCUT-HKUST Joint Research Laboratory, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

## Table of Contents

**Table S1** Solvent effect on the polymerization of **1** and **2**.

**Fig. S1** <sup>1</sup>H NMR spectrum of **3b** in chloroform-*d*.

**Fig. S2** <sup>13</sup>C NMR spectrum of **3b** in chloroform-*d*.

**Fig. S3** High-resolution mass spectrum of **3b**.

**Fig. S4** ORTEP drawing of single crystals of **3b** (CCDC 1043916).

**Table S2** Crystal data and structure refinement for model compound **3b**.

**Fig. S5** TGA thermogram of **P1/2** recorded under nitrogen at a heating rate of 10 °C/min.

**Fig. S6** DSC thermogram of **P1/2** recorded under nitrogen during the second heating cycle at a heating rate of 10 °C/min.

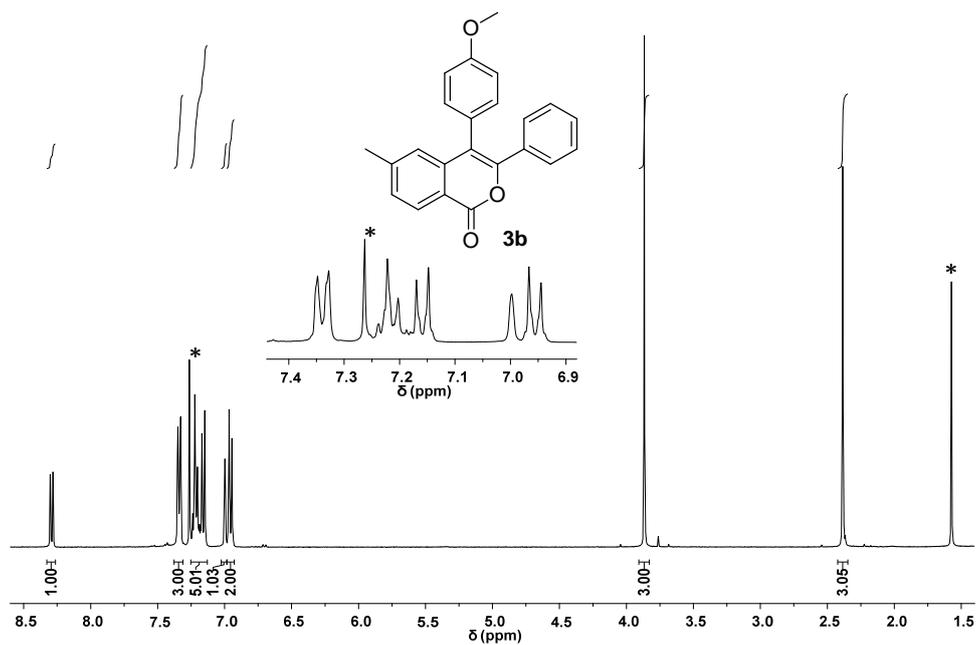
**Fig. S7** Size distributions of nanoparticles of **P1/2** suspended in THF/water mixtures with (A) 70 vol %, (B) 80 vol %, and (C) 99 vol % water fractions. Concentration: 10 μM.

**Table S3** Refractive indices and chromatic dispersions of **P1/2**.

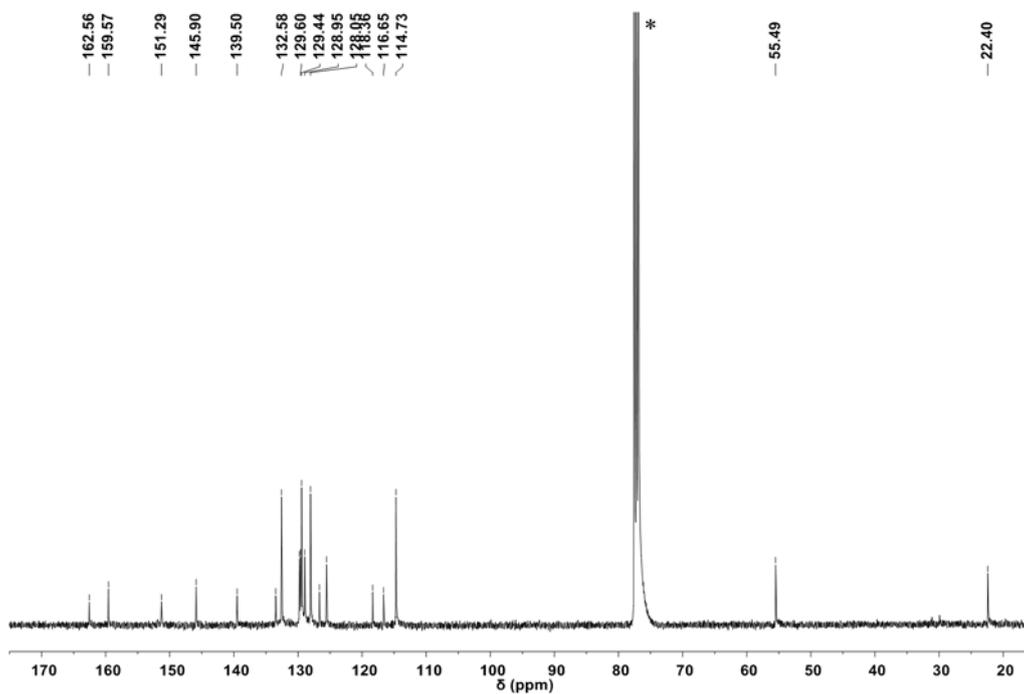
**Table S1** Solvent effect on the polymerization of **1** and **2**<sup>a</sup>

Entry	Solvent	Yield (%)	$M_w^b$	$M_w/M_n^b$
1 <sup>c</sup>	DMF	88.1	26 300	2.95
2	<i>o</i> -DCB	Trace		
3	DMSO	Trace		
4	<i>o</i> -xylene	Trace		

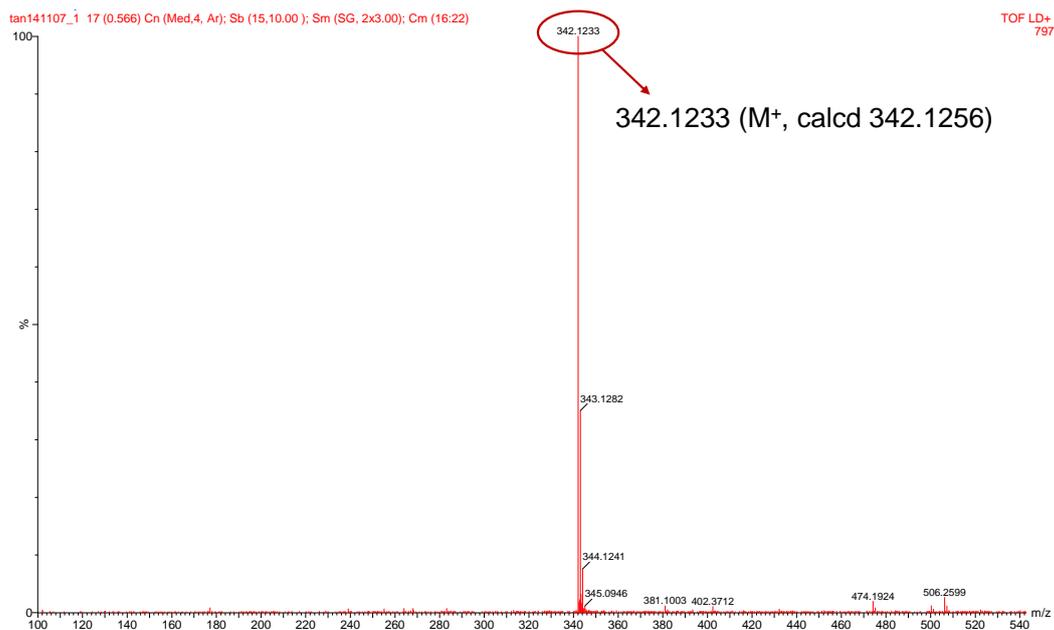
<sup>a</sup> Carried out in air at 120 °C for 24 h in the presence of [Cp\*<sub>2</sub>RhCl<sub>2</sub>]<sub>2</sub> and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O. [1] = 0.10 M, [2] = 0.10 M, [Rh] = 0.002 M, [Cu] = 0.005 M. <sup>b</sup> Determined by GPC in THF on the basis of a linear polystyrene calibration. <sup>c</sup> Data taken from Table 3, entry 2.



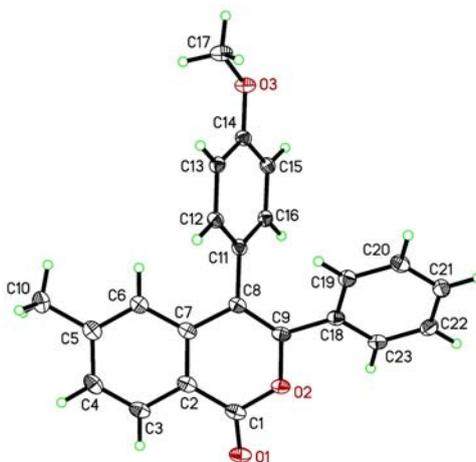
**Fig. S1** <sup>1</sup>H NMR spectrum of **3b** in chloroform-*d*.



**Fig. S2** <sup>13</sup>C NMR spectrum of **3b** in chloroform-*d*.



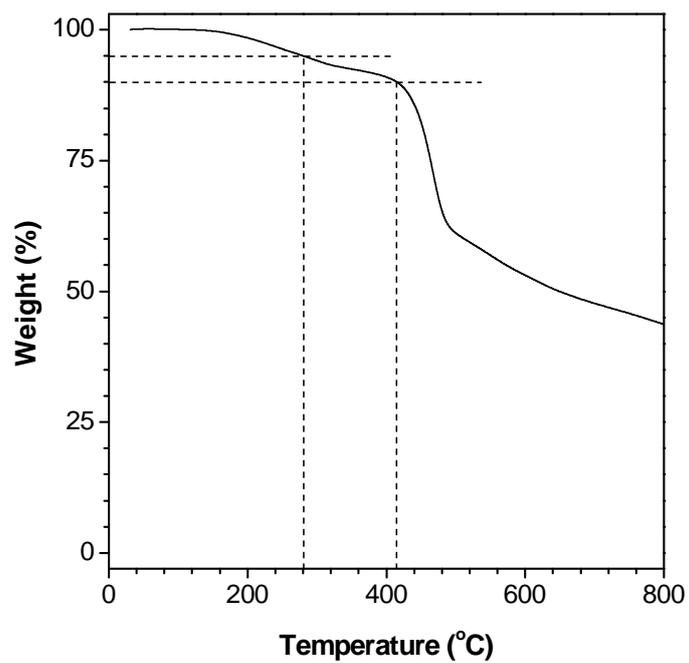
**Fig. S3** High-resolution mass spectrum of **3b**.



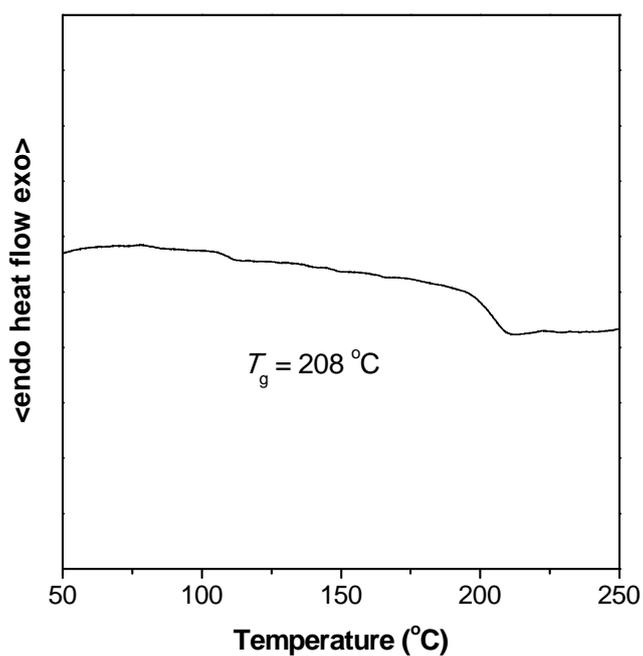
**Fig. S4** ORTEP drawing of single crystals of **3b** (CCDC 1043916).

**Table S2** Crystal data and structure refinement for model compound **3b**

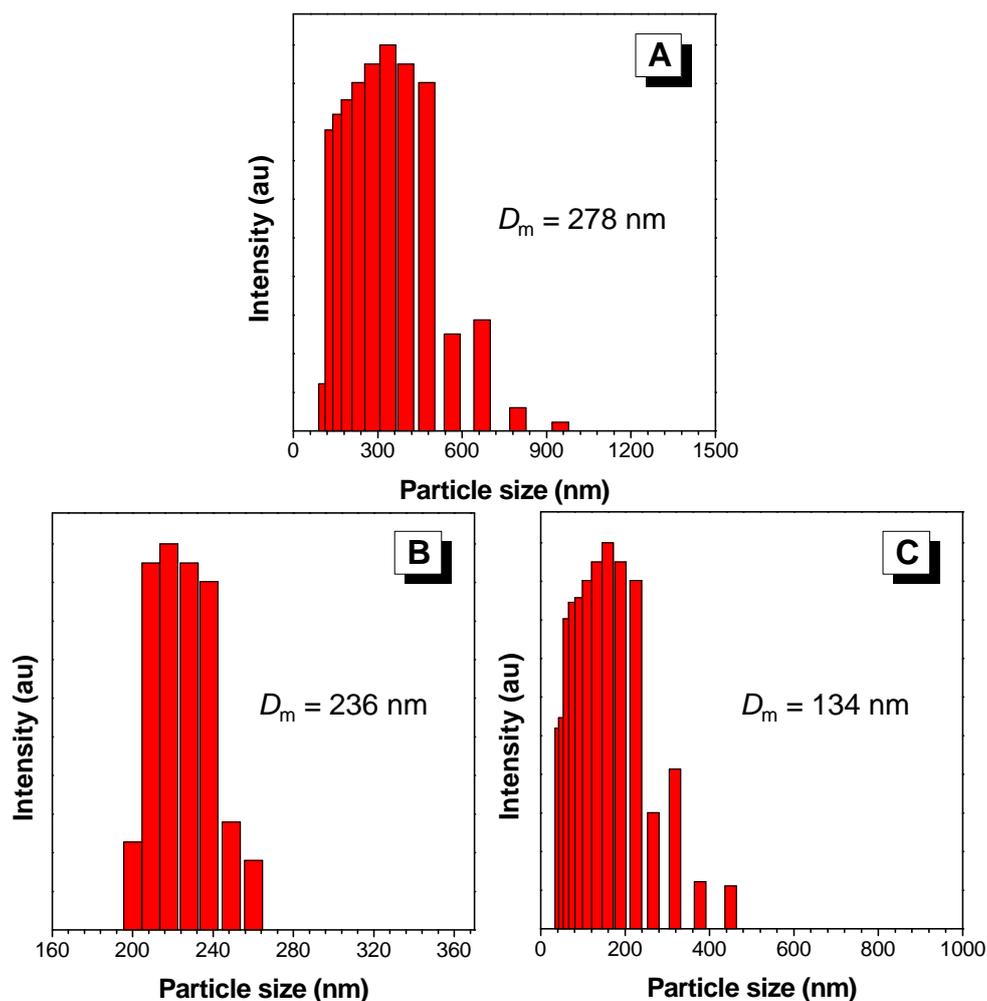
Empirical formula	C <sub>23</sub> H <sub>18</sub> O <sub>3</sub>
Formula weight	342.37
Temperature	99.9(4) K
Wavelength	1.5418 Å
Crystal system	Monoclinic
Space group	Pc
Unit cell dimensions	a = 5.82646(9) Å    α = 90°. b = 9.44106(13) Å    β = 100.1098(15)°. c = 15.6160(3) Å    γ = 90°.
Volume	845.67(2) Å <sup>3</sup>
Z, Calculated density	2, 1.345 Mg/m <sup>3</sup>
Absorption coefficient	0.707 mm <sup>-1</sup>
F(000)	360
Crystal size	0.20 x 0.18 x 0.05 mm <sup>3</sup>
Theta range for data collection	4.68 to 67.47°.
Index ranges	-6<=h<=5, -11<=k<=10, -17<=l<=18
Reflections collected	4507
Independent reflections	2180 [R(int) = 0.0120]
Completeness to theta = 66.50°	99.63%
Max. and min. transmission	1.00000 and 0.87146
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2180 / 2 / 237
Goodness-of-fit on F <sup>2</sup>	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0221, wR2 = 0.0557
R indices (all data)	R1 = 0.0222, wR2 = 0.0558
Largest diff. peak and hole	0.104 and -0.131 e.Å <sup>-3</sup>



**Fig. S5** TGA thermogram of P1/2 recorded under nitrogen at a heating rate of 10 °C/min.



**Fig. S6** DSC thermogram of P1/2 recorded under nitrogen during the second heating cycle at a heating rate of 10 °C/min.



**Fig. S7** Size distributions of nanoparticles of P1/2 suspended in THF/water mixtures with (A) 70 vol %, (B) 80 vol % and (C) 99 vol % water fractions. Concentration: 10  $\mu$ M.

**Table S3** Refractive indices and chromatic dispersions of P1/2<sup>a</sup>

Entry	Time (min)	$n_{632.8}$	$\nu_D$	$D$
1	0	1.6920	7.7333	0.1293
2	10	1.6466	15.8475	0.0631
3	30	1.6304	16.0146	0.0624
4	40	1.6174	17.9358	0.0558

<sup>a</sup> Abbreviation:  $n$  = refractive index,  $\nu_D$  = Abbé number =  $(n_D - 1)/(n_F - n_C)$ , where  $n_D$ ,  $n_F$  and  $n_C$  are the  $n$  values at wavelengths of Fraunhofer D, F and C spectral lines of 589.2, 486.1 and 656.3 nm, respectively;  $D$  = chromatic dispersion =  $1/\nu_D$ .