Rational molecular and doping strategies for winning ultra-long-lived organic RTP polymers

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Materials

Polyvinyl alcohol (PVA) was purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China, PVA: alcoholysis degree: 78.5–81.5%, viscosity index:45.0-51.0 mPa.s). All other chemicals and solvents were purchased from Energy Chemical Co., Ltd (Shanghai, China) and used with further purification.

General method

¹H spectra was recorded on AC500 spectrometer at 500 MHz, using deuterated chloroform or deuterated dimethyl sulfoxide as the solvent and tetramethylsilane (TMS) as the internal standard(Bruker, Germany). Photo-fluorescence and phosphorescence emission spectra were recorded on F-4600 spectrophotometers(Hitachi, Japan). Absolute PL quantum yields (PLQY) were

determined with a spectrometer C11347 (Hamamatsu, Japan). Fluorescence and phosphorescence decay curves were recorded by FLS-1000 fluorescence lifetime spectrometer (Edinburgh Instruments, The United Kingdom). The lifetimes (τ) of the luminescence were obtained by fitting the decay curve with a multi-exponential decay function of

$$R(t) = \sum_{i} B_{i} e^{-\frac{t}{\tau}}$$
(S1)

where B_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.

The PL photographs were captured by the FDR-AX700 4K HDR digital cameras (SONY, Japan), and the excitation intensity was 0.3 mW/cm². Photoluminescence spectra and photographs at room temperature were performed on a QE Pro spectrometer with a CCD array (Ocean Optics) as a power detector.

Purification, synthesis and films preparation

Purification

(9-phenyl-carbazol-2-yl)-boric acid (C2BA). C2BA was purchased from Energy Chemical Co., Ltd (Shanghai, China) and used with further purification. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.21 (d, J = 7.7 Hz, 1H), 7.86 (dd, J = 8.3, 1.2 Hz, 1H), 7.66 – 7.59 (m, 4H), 7.52 – 7.48 (m, 1H), 7.44 – 7.39 (m, 3H), 7.32 (ddd, J = 8.0, 4.7, 3.3 Hz, 1H), 2.05 (t, J = 5.5 Hz, 2H).

4-(9H-carbazol-9-yl) boronic acid(P4BA). P4BA was purchased from Energy Chemical Co., Ltd (Shanghai, China) and used with further purification. ¹H NMR

(500 MHz, DMSO-*d*₆) δ 8.26 (d, J = 6.7 Hz, 4H), 8.12 – 8.06 (m, 2H), 7.64 – 7.58 (m, 2H), 7.47 – 7.41 (m, 4H), 7.31 (ddd, J = 7.9, 6.1, 1.9 Hz, 2H).

3-(9H-carbazol-9-yl) boronic acid(P3BA). It was purchased from Energy Chemical Co., Ltd (Shanghai, China) and used with further purification. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.32 – 8.24 (m, 4H), 8.00 (s, 1H), 7.95 (t, J = 4.3 Hz, 1H), 7.67 (d, J = 4.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H). **2-(9H-carbazol-9-yl) boronic acid(P2BA).** It was purchased from Energy Chemical Co., Ltd (Shanghai, China) and used with further purification. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.20 (d, J = 7.7 Hz, 2H), 7.82 (d, J = 7.4 Hz, 1H), 7.72 (s, 2H), 7.64 (dd, J = 8.5, 6.8 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.25 – 7.17 (m, 4H). **Synthesis**

C2BE.



Scheme S1. Synthetic route of C2BE.

Stir a mixture of C2BA (3.48 mmol), 1,3-propylenediol (4.18 mmol), 0.42 g of MgSO₄ (3.48 mmol) and 20 mL of dichloromethane for 20 hours at room temperature under a N_2 atmosphere. Then filter the reaction mixture. Wash the reaction mixture with dichloromethane. Dry the organic phase over anhydrous MgSO₄. Purify the mixture by flash chromatography on a silica gel column using dichloromethane as an

eluent to obtain C2BE. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.56 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.70 (t, J = 7.7 Hz, 2H), 7.65 – 7.62 (m, 2H), 7.57 (d, J = 7.3 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.31 (dd, J = 14.0, 6.5 Hz, 2H), 4.17 (t, J = 5.4 Hz, 4H), 2.06 (p, J = 5.3 Hz, 2H). Anal. calcd. For C21H18BNO2: C, 77.09; H, 5.55; B, 3.30; N, 4.28; O, 9.78; found: C, 77.12; H, 5.58; B, 3.27; N, 4.29; O, 9.80.

Preparation of PVA films.

Prepare 150 mL of 5 g PVA aqueous solution and then slowly add 15 mL of *N*-phenylcarbazole derivatives ethanol solution via a controllable syringe under electromagnetic stirring to form the mixtures containing 2.0–0.01 wt% *N*-phenylcarbazole derivatives. Aqueous mixtures are poured into a large culture dish and evaporated on 60 °C hot plate. The dried film is taken out and further dried in oven at 80–100 °C for 12 h. Then thermoplasticize these solution-cast films were thermoplasicized on an open two-roll mill for 2–3 min at 140 °C. Then, the films were cut into a 2.5cm×2.5cm square with a weight of 1.5 g, put into a mold, preheated in a flat vulcanizer for 3 min at 185 °C, and then hot-pressed under a pressure of 5 MPa for 3 min at 185 °C , and then cold-pressed for 3 min to obtain a square film with a shape of 3 cm × 3 cm and a thickness of 1 mm.

Supplementary Figures and Tables



Figure S1 The PL photographs of C2BA, P2BA, P3BA, and P4BA crystal after purification





Figure S2 The PL photographs of 1.0 wt % P2BA, P3BA and P4BA doped PVA films before and

after removing 365 nm light (0.3 mW/cm²) excitation for 5 s at room temperature in the dark.



Figure S3 The time-resolved RTP decay curves and fitted RTP lifetimes of 0.1 wt % P4BA/PVA

film monitored at 460 nm emission.



Figure S4 Emission spectra and efficiency of 1.0-0.01 wt% C2BA/PVA films measured by a

luminescent integrating sphere.



Figure S5 The time-resolved RTP decay curves and fitted RTP lifetimes of 1.0 wt % C2BE/PVA

film monitored at 460 nm emission.



Figure S6 The PL spectrum and quantum yield of C2BA/PVA, C2BA/RB/PVA and RB/PVA

films under 365 nm light excitation measured by an integrating sphere.

Doped in PVA	$ au_1, s(\%)$	$ au_2, s(\%)$	$\tau_3, s(\%)$	<\alpha>, s
0.01% C2BA	0.068(1.8%)	0.580(8.5%)	3.517(89.7%)	3.155
0.1% C2BA	0.721(4.1%)	4.444(95.9%)	-	4.291
0.5% C2BA	1.040(4.1%)	3.875(95.9%)	-	3.759
1.0% C2BA	0.928(4.8%)	3.712(95.2%)	-	3.578

Table S1 Fitted component lifetimes and ratios of 1.0-0.01 wt% C2BA/PVA films

¹H NMR







Figure S10 ¹H spectrum of P2BA in DMSO-*d*₆.



9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 fl (ppm)

Figure S11 ¹H spectrum of P3BA in DMSO-d₆.



Figure S13 ¹H spectrum of C2BE in DMSO-*d*₆.