Supporting Information

for

Bipyridinium radical cation dimerization-driven polymeric pleated foldamers and homoplex that undergo ion-tuned interconversion

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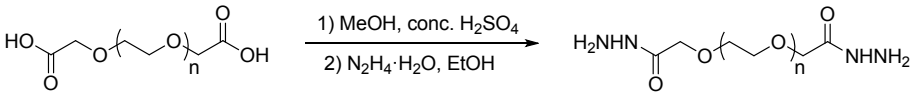
Contents:

Synthesis of Dihydrazone 2a-d:



1a: n = 1
1b: n = 2
1c: n = 3
1d: n = 4

2a: n = 1
2b: n = 2
2c: n = 3
2d: n = 4

Compounds **1a-d**[1] and **M1**[2] were all prepared according to reported procedures.

Compound 2a. To a solution of diacid **1a** (0.18 g, 1.00 mmol) in methanol (20 mL) was added concentrated sulfuric acid (98%, 0.5 mL) slowly. The solution was stirred under reflux for 12 h and then cooled to room temperature. The solution was neutralized with saturated sodium bicarbonate solution to pH 7 and then the mixture was concentrated with a rotavapor. The resulting slurry was triturated with dichloromethane (50 mL). The organic solution was washed with water (20 mL) and brine (25 mL), and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure afforded the corresponding diester as a pale yellow oil (0.21 g, 100%). The obtained oil was dissolved in ethanol (20 mL). To the solution was added hydrazine monohydrate (98%, 2.0 mL). The solution was stirred under reflux for 3 h and then concentrated under reduced pressure to give compound **2a** as a white solid (0.19 g, 94 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.97 (s, 2 H), 4.28 (s, 4 H), 3.90 (s, 4 H), 3.57 (s, 4 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.1, 70.1, 69.4; HRMS (ESI): Calcd. for $C_6H_{15}N_4O_4$: 207.1093 $[M+H]^+$. Found: 207.1098.

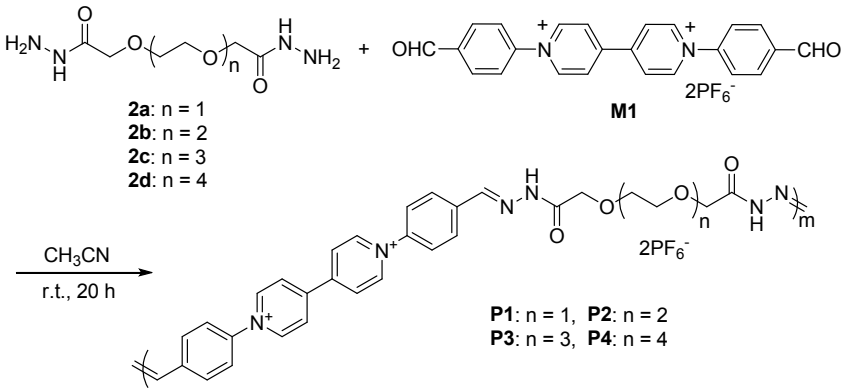
Compounds **2b-d** were prepared from compounds **1b-d**, following the procedure described for **2a**.

Compound 2b. Pale yellow solid (91%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.90 (s, 4H), 3.56 (s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.3, 70.4, 69.6, 69.5; HRMS (ESI): Calcd for $C_8H_{19}N_4O_5$: 251.1355 $[M+H]^+$. Found: 251.1358.

Compound 2c. Pale yellow solid (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (br, 2H), 4.78 (s, 4H), 4.04 (s, 4H), 3.72-3.55 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 71.1, 70.5, 70.2, 70.1; HRMS (ESI): Calcd for $C_{10}H_{23}N_4O_6$: 295.1618 $[M+H]^+$. Found: 295.1600.

Compound 2d. Pale yellow oil (92 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.89 (s, 4H), 3.58-3.48 (m, 16H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.2, 70.3, 69.8, 69.6, 69.4; HRMS (ESI): Calcd. for $C_{12}H_{27}N_4O_7$: 339.1880 $[M+H]^+$. Found: 339.1880.

Synthesis of polymers P1-P4:



2a: n = 1
2b: n = 2
2c: n = 3
2d: n = 4

M1

P1: n = 1, **P2**: n = 2
P3: n = 3, **P4**: n = 4

Polymer P1: Compound **M1** (30 mg, 0.046 mmol) was dissolved in acetonitrile (5 mL). To the solution was added dropwise a solution of compound **2a** (9.5 mg, 0.046 mmol) in acetonitrile (5 mL). The mixture was stirred at room temperature for 20 h and then the solvent was removed with a rotavapor. The resulting residue was suspended in 0.5 mL of dichloromethane and ether (1:1). The solid was filtrated and washed with ether, and dried in vacuo to give polymer **P1** as a dark orange solid (37 mg, 94%).

Polymers **P2-P4** were prepared from the reactions of **2b-2d** and **M1** in 95%, 92%, and 95% yields, respectively, according to the procedure described for polymer **P1**.

Because Gel Permeation Chromatography (GPC) cannot determine the average molecular weight of these polymers, ^{1}H NMR spectroscopy has been used to estimate the degree of polymerization of the polymers. ^{1}H NMR spectra of polymers **P1-P4** showed no signal of the O=C*H* proton. Considering the resolution of the ^{1}H NMR technique, we assumed that at least 95% of the aldehyde group had been converted into the hydrazone group.[3] On the basis of this assumption, we could estimate the degree of polymerization of the polymers to be 10:

$$\mathrm{DP} = \frac{1}{2}\left[\frac{\int \text{Hydrazone } {}^1\text{H}}{\int \text{Terminal Aldehyde } {}^1\text{H}} + 1\right]$$

References:

1. V. Wittmann, S. Takayama, K. W. Gong, G. Weitz-Schmidt and C.-H. Wong, *J. Org. Chem.*, 1998, **63**, 5137.
2. L. Chen, H. Wang, D.-W. Zhang, Y. Zhou and Z.-T. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 4028.
3. (*a*) W. G. Skene and J.- M. Lehn, *Proc. Natl. Acad. Sci. USA*, 2004, **101**, 8270; (*b*) Y.-C. Zhang, Y. M. Zhou, Z.-T. Li and D.-W. Zhang, *Tetrahedron*, 2015, **71**, 605.

^{1}H NMR spectra of polymers P1-P4:

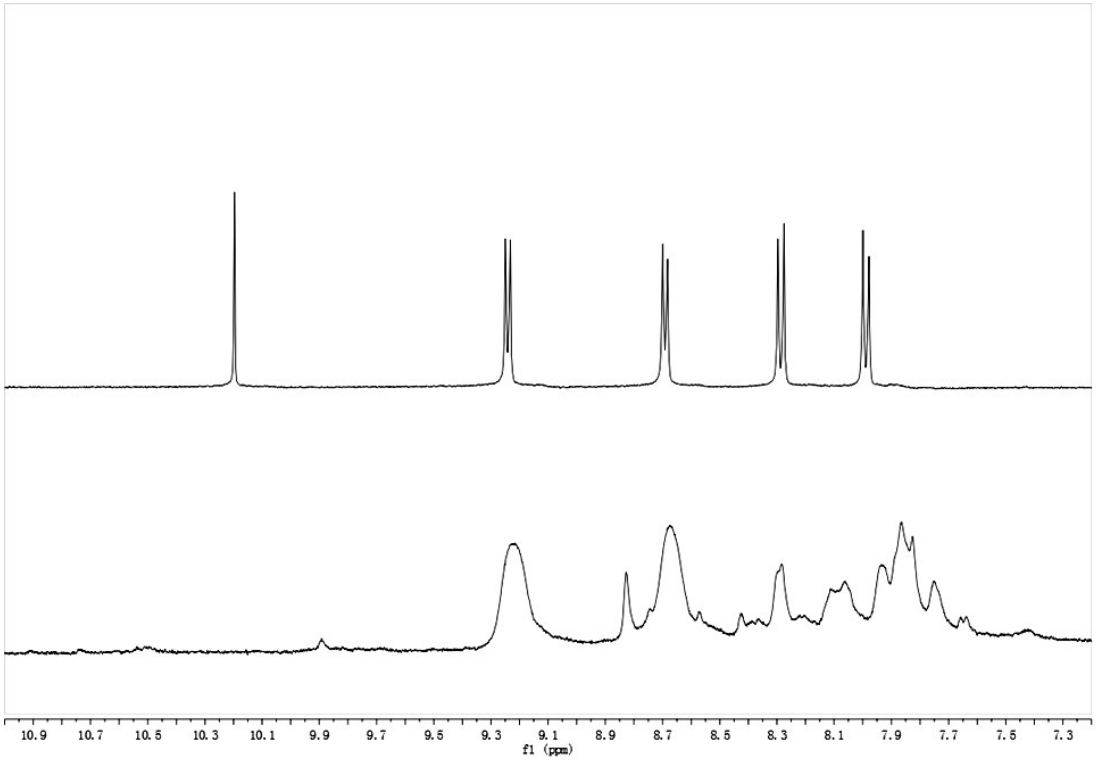


Fig. S1 ^{1}H NMR spectrum (400 MHz) of (down) polymer **P1** ([BIPY] = 2.0 mM) and (top) compound **M1** (2.0 mM) in CD_3CN at 25 °C.

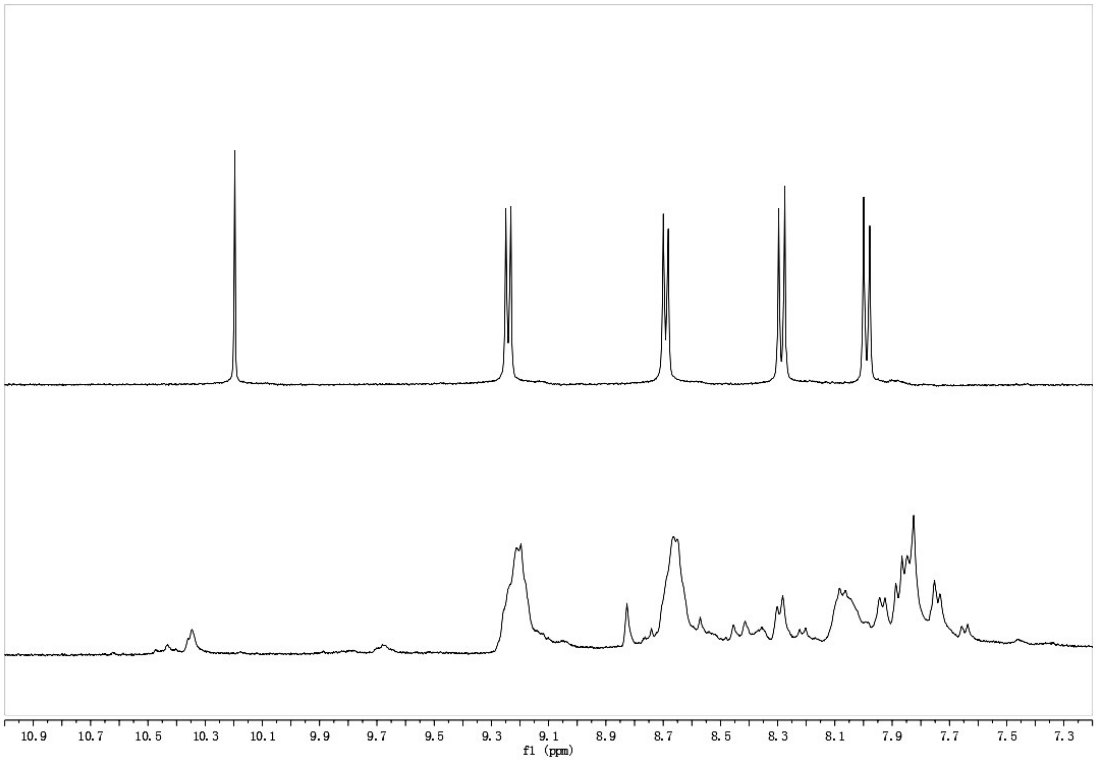


Fig. S2 ^{1}H NMR spectrum (400 MHz) of (down) polymer **P2** ([BIPY] = 2.0 mM) and (top) compound **M1** (2.0 mM) in CD_3CN at 25 °C.

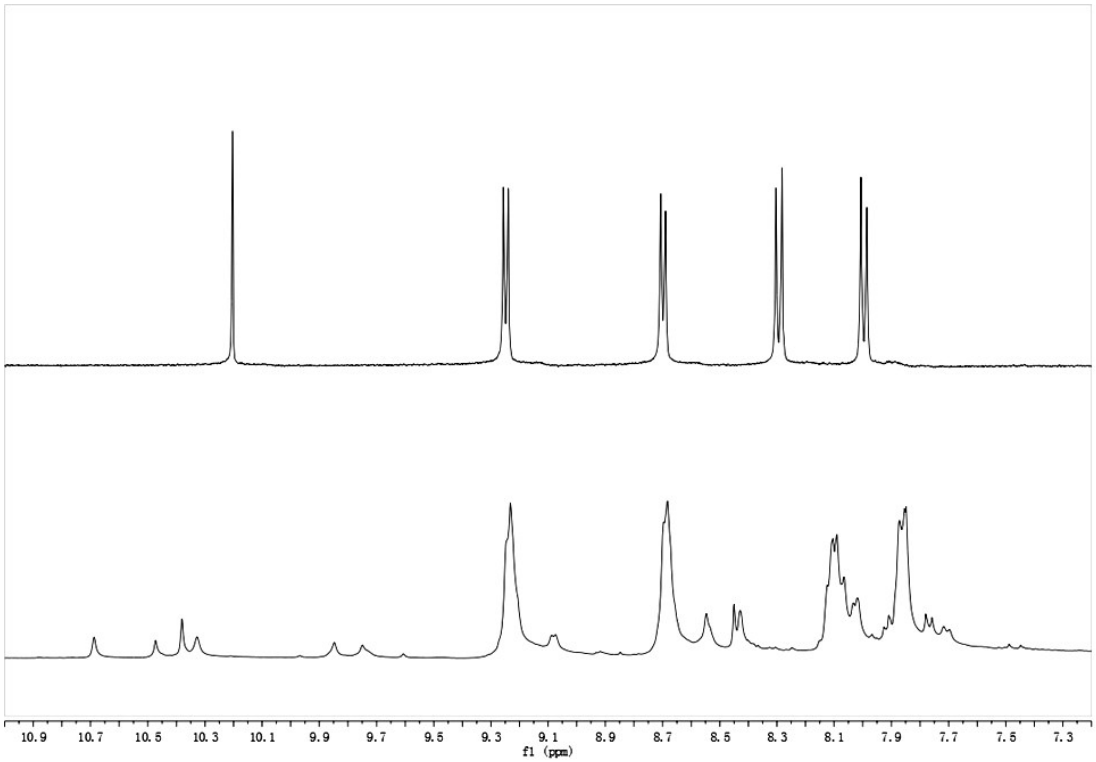


Fig. S3 ^{1}H NMR spectrum (400 MHz) of (down) polymer **P3** ([BIPY] = 2.0 mM) and (top) compound **M1** (2.0 mM) in CD_3CN at 25 °C.

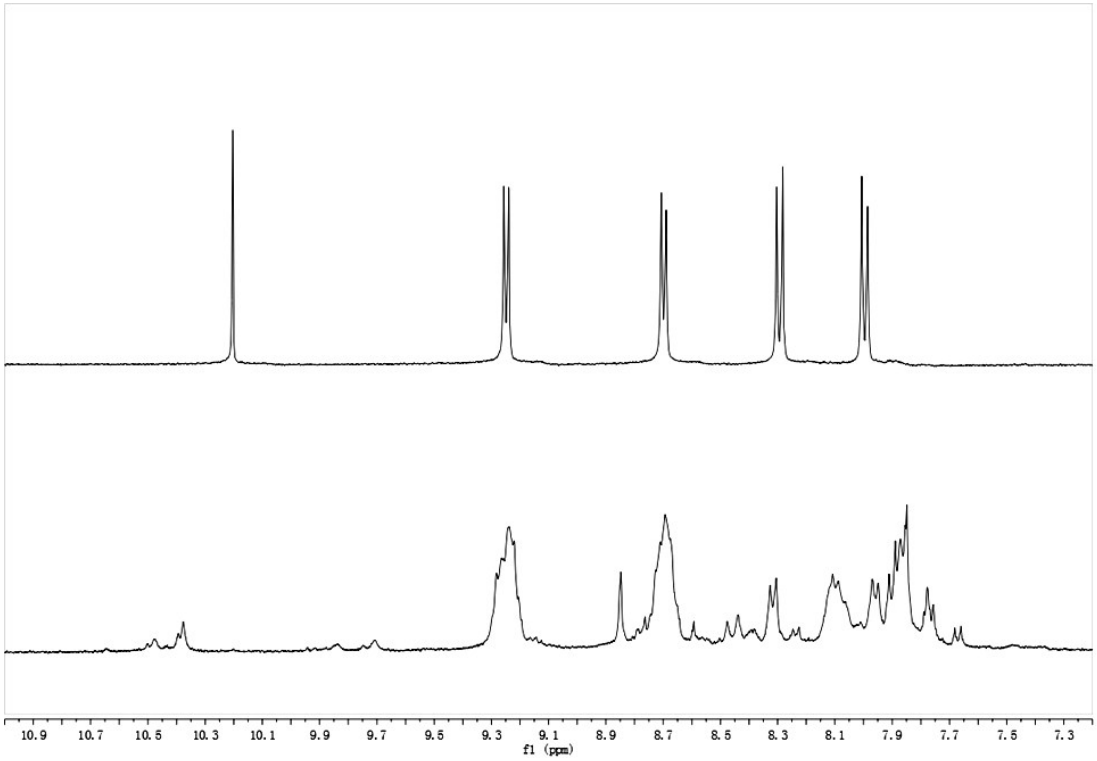


Fig. S4 ^{1}H NMR spectrum (400 MHz) of (down) polymer **P4** ([BIPY] = 2.0 mM) and (top) compound **M1** (2.0 mM) in CD_3CN at 25 °C.

Absorption spectroscopy studies:

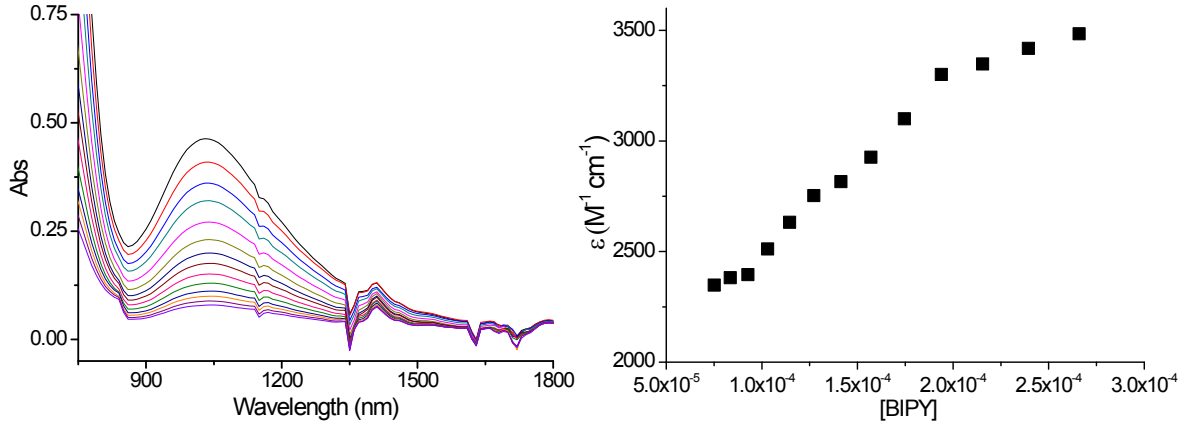


Fig. S5 Left: Absorption spectra of **P1** ([BIPY] = 0.27-0.075 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Right: Plot of ε (1038 cm) versus [BIPY].

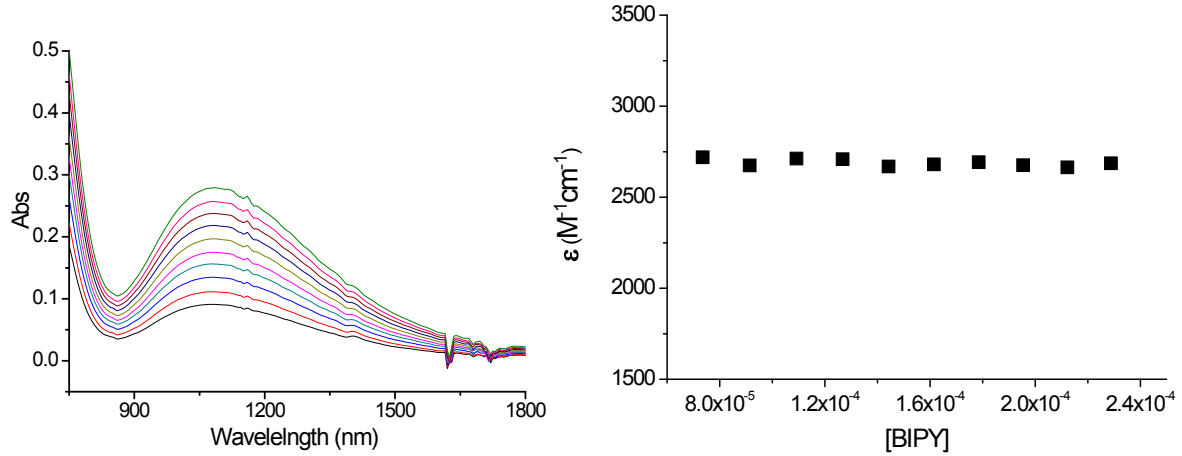


Fig. S6 Left: Absorption spectra of **P2** ([BIPY] = 0.23-0.074 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Right: Plot of ε (1080 cm) versus [BIPY].

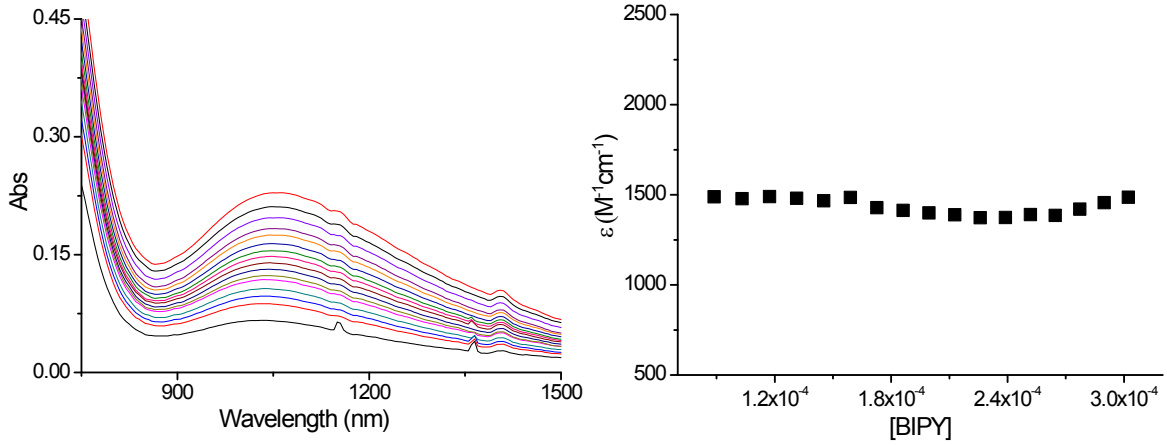


Fig. S7 Left: Absorption spectra of **P3** ([BIPY] = 0.30–0.08 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Right: Plot of ε (1053 cm) versus [BIPY].

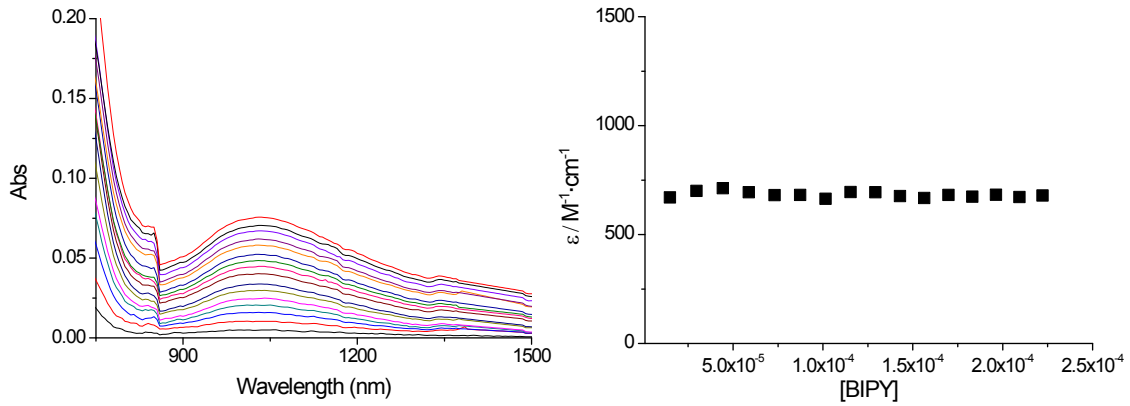


Fig. S8 Left: Absorption spectra of **P4** ([BIPY] = 0.22-0.015 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Right: Plot of ε (1030 cm) versus [BIPY].

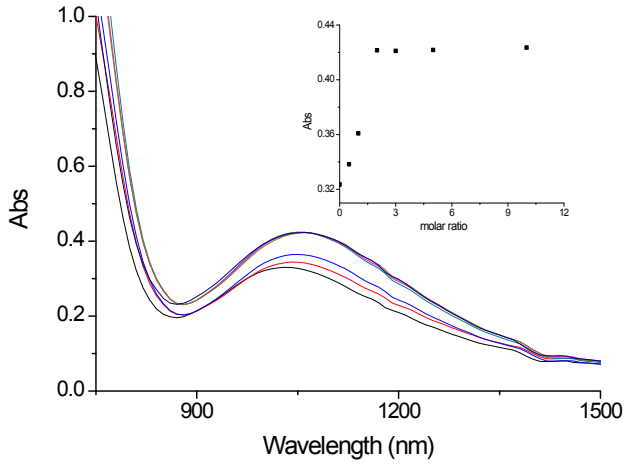


Fig. S9 Absorption spectrum of polymer **P1** ([BIPY] = 0.2 mM) recorded after the addition of NH_4PF_6 in CH_3CN at 25 °C. Reducing agent: activated zinc dust. Inset: Absorption (λ_{max}) vs $[NH_4PF_6]/[BIPY]$.

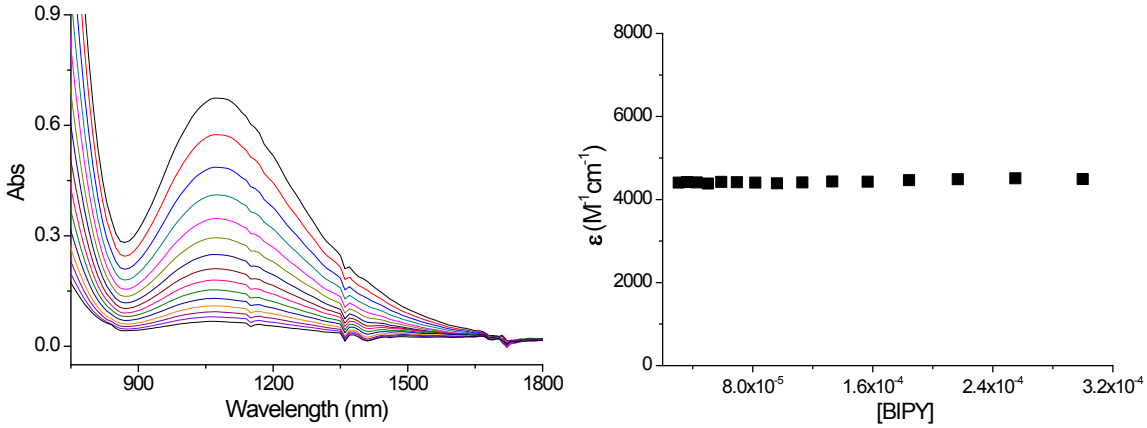


Fig. S10 Left: Absorption spectra of the mixture of **P1** and $LiPF_6$ (1:1) ([BIPY] = $[LiPF_6]$ = 0.3-0.03 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Right: Plot of ε (1065 cm) versus [BIPY].

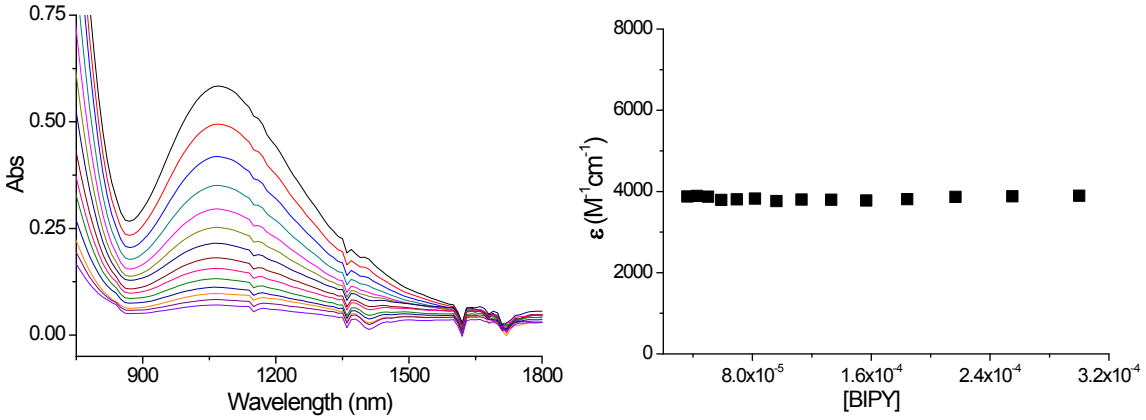


Fig. S11 Left: Absorption spectra of the mixture of **P1** and $NaPF_6$ (1:1) ([BIPY] = [$NaPF_6$] = 0.3-0.03 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Right: Plot of ε (1065 cm) versus [BIPY].

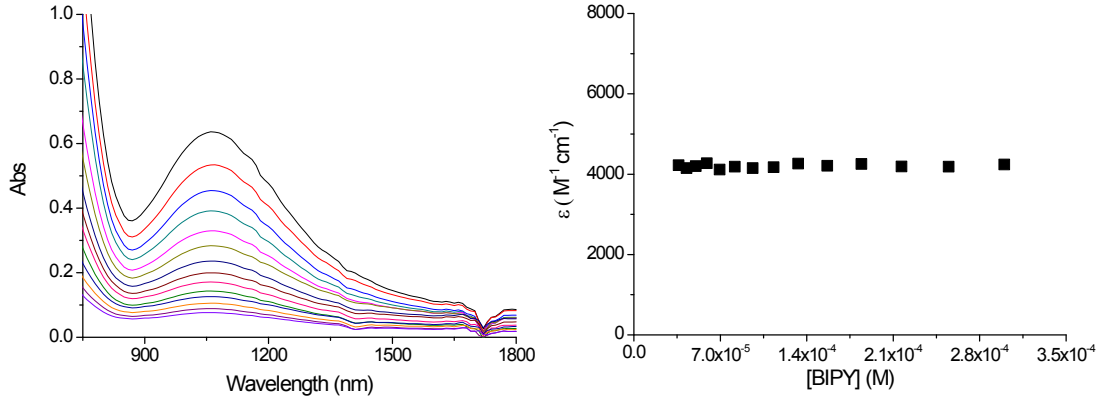


Fig. S12 Left: Absorption dilution spectra of the solution of polymer **P1** and NH_4PF_6 (1:1) ([BIPY] = [NH_4PF_6] = 0.30-0.036 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Right: Plot of ε (1065 cm) versus [BIPY].

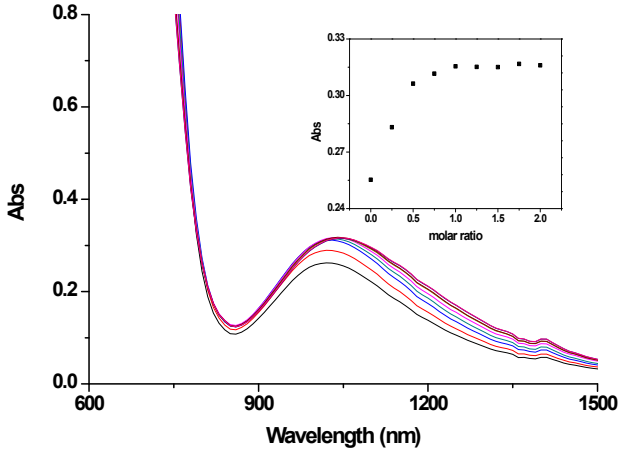


Fig. S13 Absorption spectrum of polymer **P2** ([BIPY] = 0.2 mM) recorded after the addition of $LiPF_6$ in CH_3CN at 25 °C. Reduction agent: activated zinc dust. Inset: Absorption (λ_{max}) vs [$LiPF_6$]/[BIPY].

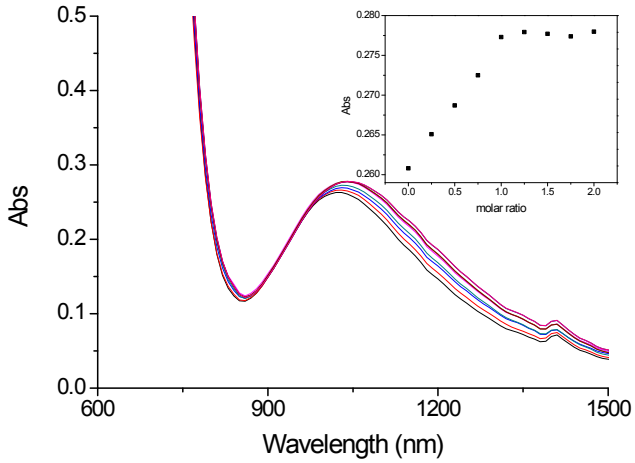


Fig. S14 Absorption spectrum of polymer **P2** ([BIPY] = 0.2 mM) recorded after the addition of $NaPF_6$ in CH_3CN at 25 °C. Reducing agent: activated zinc dust. Inset: Absorption (λ_{max}) vs [$NaPF_6$]/[BIPY].

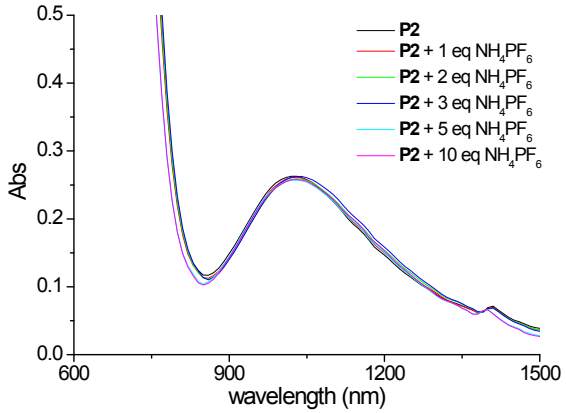


Fig. S15 Absorption spectrum of polymer **P2** ([BIPY] = 0.2 mM) recorded after the addition of NH_4PF_6 in CH_3CN at 25 °C. Reducing agent: activated zinc dust.

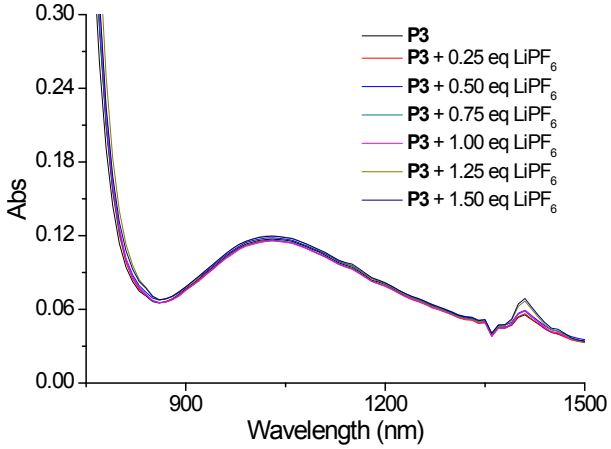


Fig. S16 Absorption spectrum of polymer **P3** ([BIPY] = 0.2 mM) recorded after the addition of $LiPF_6$ in CH_3CN at 25 °C. Reducing agent: activated zinc dust.

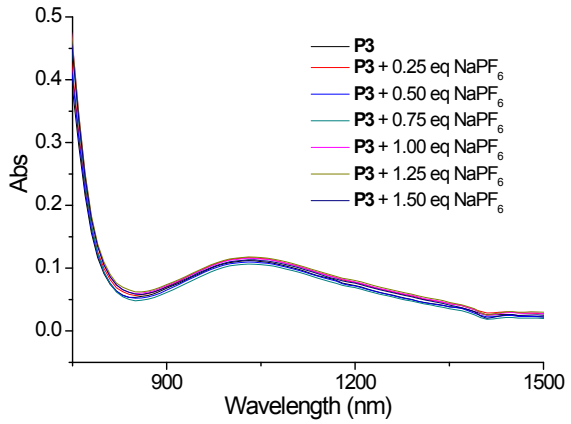


Fig. S17 Absorption spectrum of polymer **P3** ([BIPY] = 0.2 mM) recorded after the addition of $NaPF_6$ in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

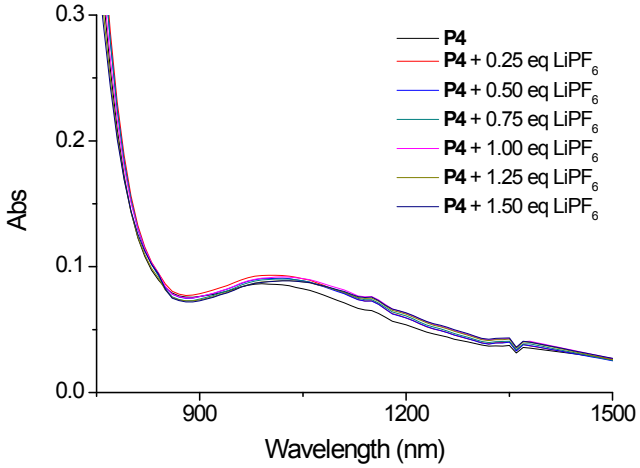


Fig. S18 Absorption spectrum of polymer **P4** ([BIPY] = 0.2 mM) recorded after the addition of $LiPF_6$ in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

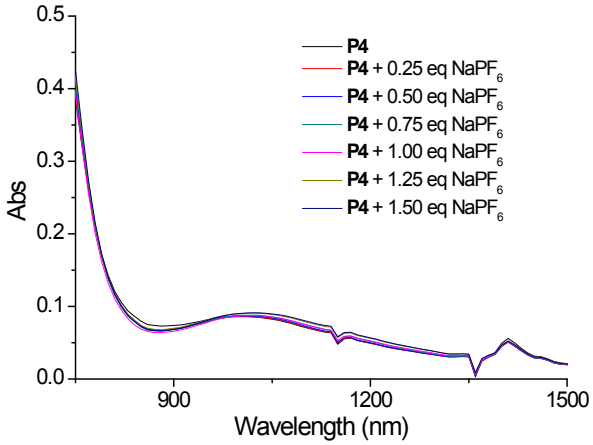


Fig. S19 Absorption spectrum of polymer **P4** ([BIPY] = 0.2 mM) recorded after the addition of $NaPF_6$ in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

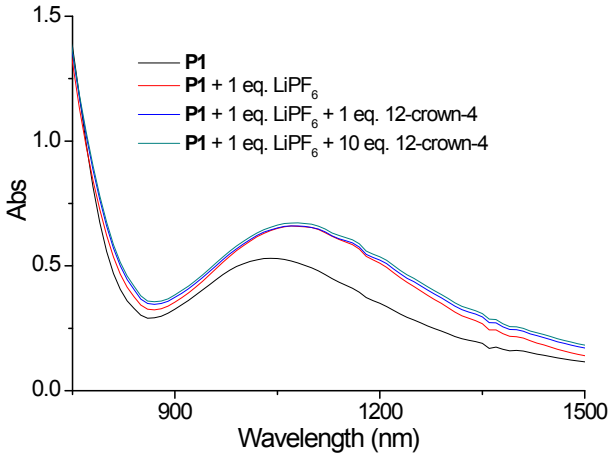


Fig. S20 Absorption spectra of polymer **P1** ([BIPY] = 0.3 mM) in acetonitrile at 25 °C with the addition of $LiPF_6$ and further addition of 12-crown-4. Reduction agent: activated zinc dust.

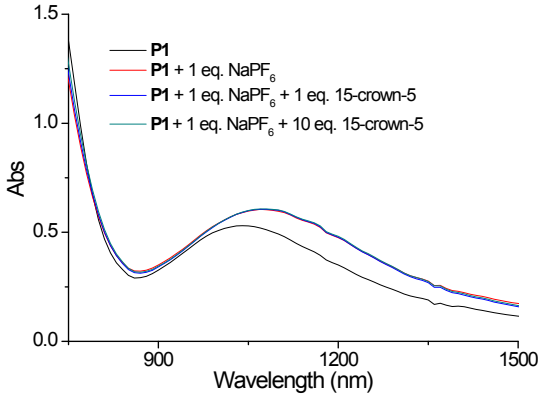


Fig. S21 Absorption spectra of polymer **P1** ([BIPY] = 0.3 mM) in acetonitrile at 25 °C with the addition of $NaPF_6$ and further addition of 15-crown-5. Reduction agent: activated zinc dust.

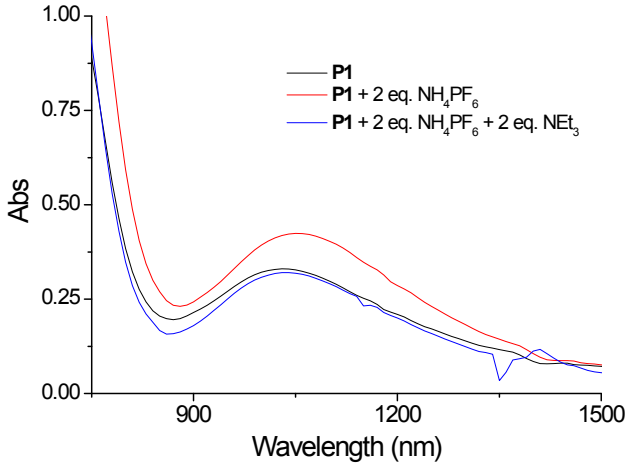


Fig. S22 Absorption spectrum of polymer **P1** ([BIPY] = 0.2 mM) recorded after the addition of NH_4PF_6 and further addition of NEt_3 in CH_3CN at 25 °C. Reducing agent: activated zinc dust.

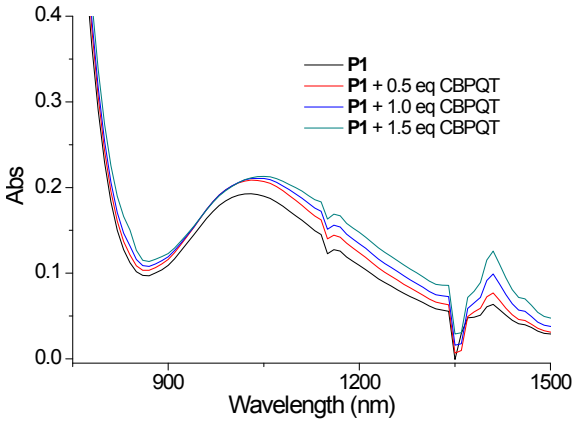


Fig. S23 Absorption spectra of **P1** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ of different amount in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

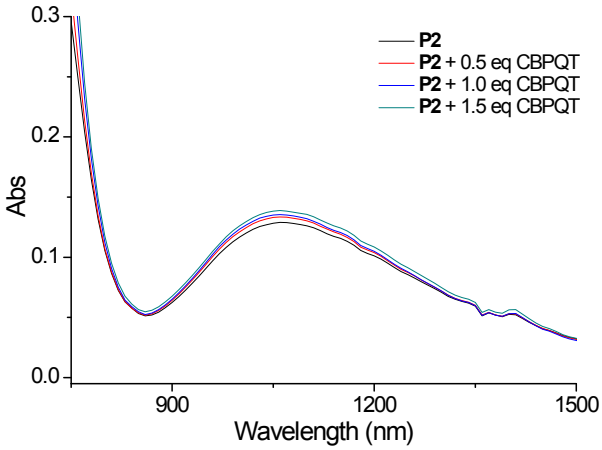


Fig. S24 Absorption spectra of **P2** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ of different amount in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

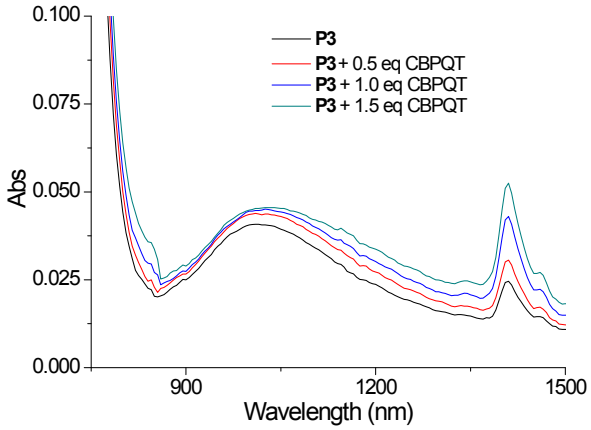


Fig. S25 Absorption spectra of **P3** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ of different amount in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

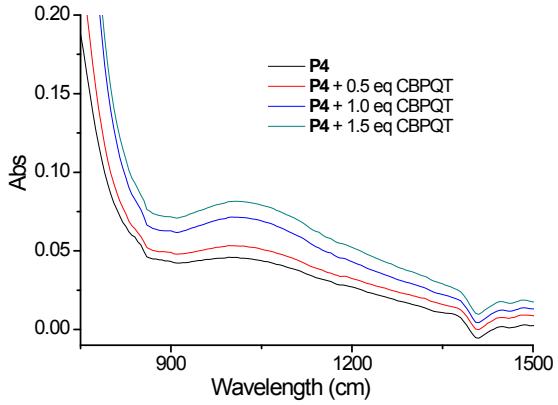


Fig. S26 Absorption spectra of **P4** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ of different amount in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

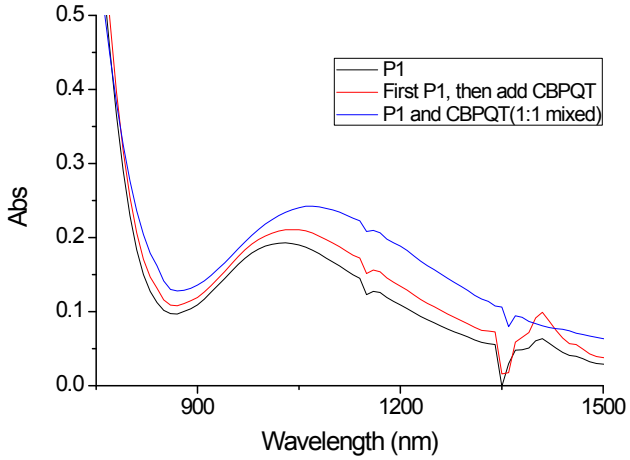


Fig. S27 Absorption spectra of **P1** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ added in different order in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

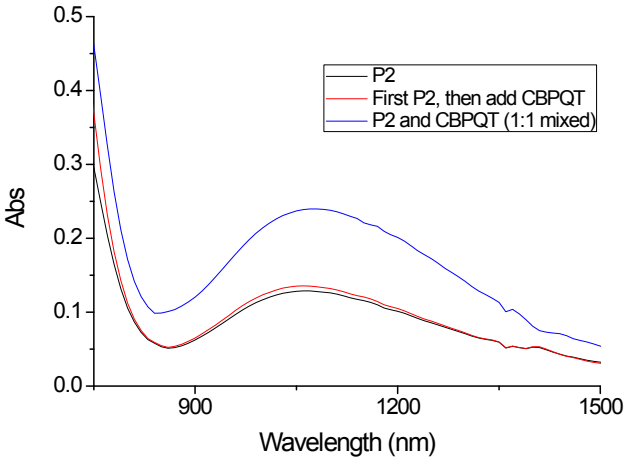


Fig. S28 Absorption spectra of **P2** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ added in different order in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

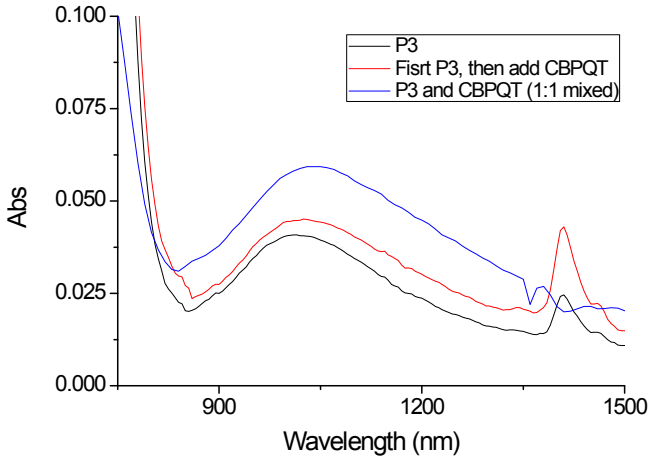


Fig. S29 Absorption spectra of **P3** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ added in different order in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

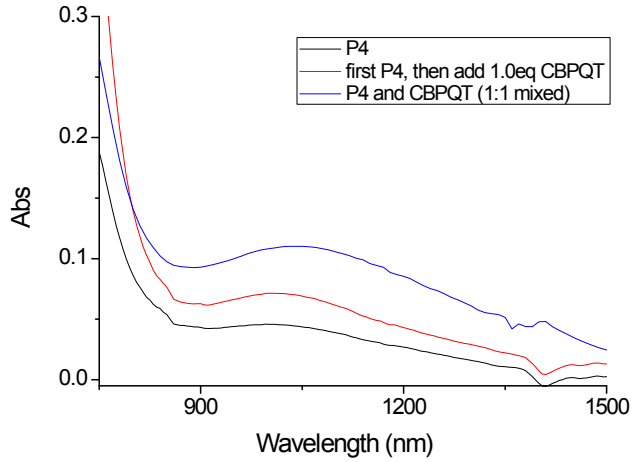


Fig. S30 Absorption spectra of **P4** ([BIPY] = 0.1 mM) with $CBPQT^{4+}4PF_6^-$ added in different order in CH_3CN at 25 °C. Reduction agent: activated zinc dust.

Electron paramagnetic resonance (EPR) studies:

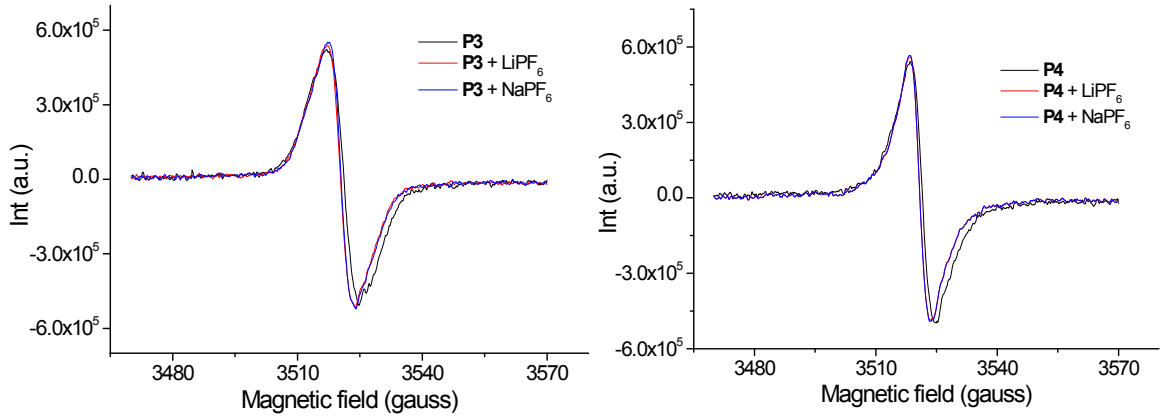


Fig. S31 Left: EPR spectrum of the solution of **P3**, **P3**/$LiPF_6$, and **P3**/$NaPF_6$ ([BIPY] = [$LiPF_6$] = [$NaPF_6$] = 0.2 mM) in CH_3CN at 25 °C. Right: EPR spectrum of **P4**, **P4**/$LiPF_6$, and **P4**/$NaPF_6$ ([BIPY] = [$LiPF_6$] = [$NaPF_6$] = 0.2 mM) in CH_3CN at 25 °C. Reduction agent: activated zinc dust.