Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Ultrafast Photoinduced Electron Transfer in Conjugated Polyelectrolyte-Acceptor Ion Pair Complexes

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I. Experimental section

Materials

All starting materials, methyl viologen (**MV**$^{2+}$) and reagents were obtained from commercial sources (Sigma-Aldrich, Fisher Scientific) and used without further purification. Conjugated polyelectrolyte (**CPE**),[1] and the electron acceptors **NDI**$^{2+}$ and **NMI**$^{+}$ were synthesized by following reported procedure.[2]

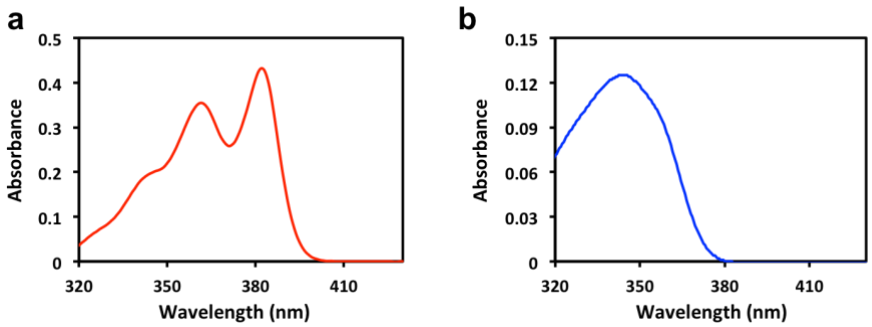

Fig. S1 Absorption spectra of (a) **NDI**$^{2+}$ and (b) **NMI**$^{+}$ in H_2O.

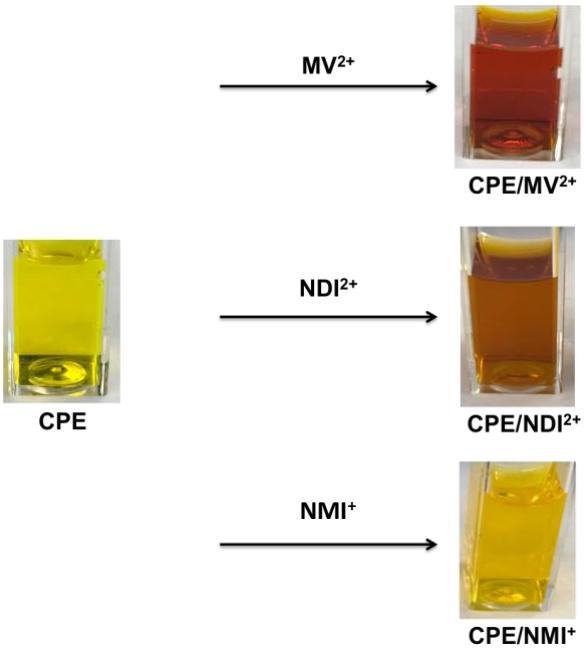

Fig. S2 Photograph of **CPE**, **CPE**/$\mathbf{MV}^{2+}$, **CPE**/$\mathbf{NDI}^{2+}$ and **CPE**/$\mathbf{NMI}^{+}$ solutions in H_2O. [**CPE**] = 1 mM in polymer repeat unit (PRU). [$\mathbf{MV}^{2+}$], [$\mathbf{NDI}^{2+}$] and [$\mathbf{NMI}^{2+}$] = 1 mM.

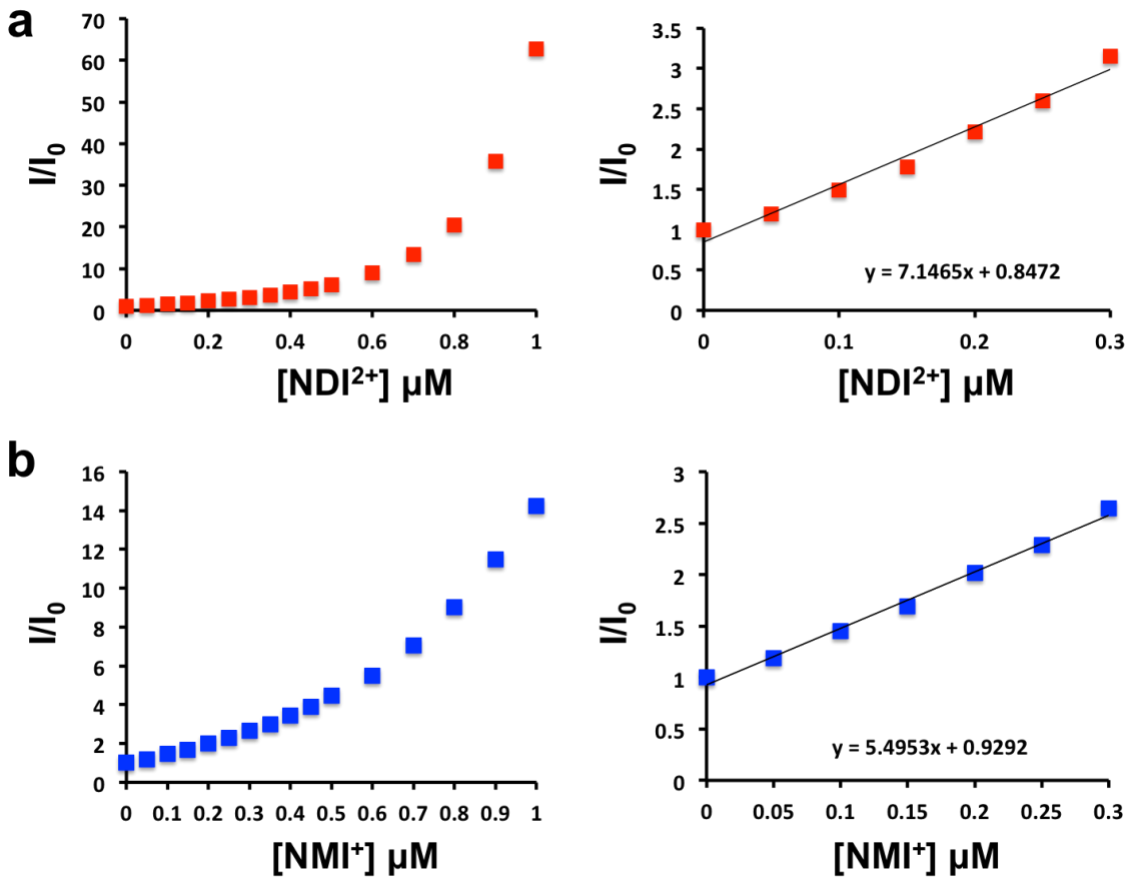

Fig. S3 Stern-Volmer plot for fluorescence quenching of **CPE** by (a) $\mathbf{NDI}^{2+}$ and (b) $\mathbf{NMI}^{+}$ in H_2O. [**CPE**] = 5.0 μM in polymer repeat unit (PRU).

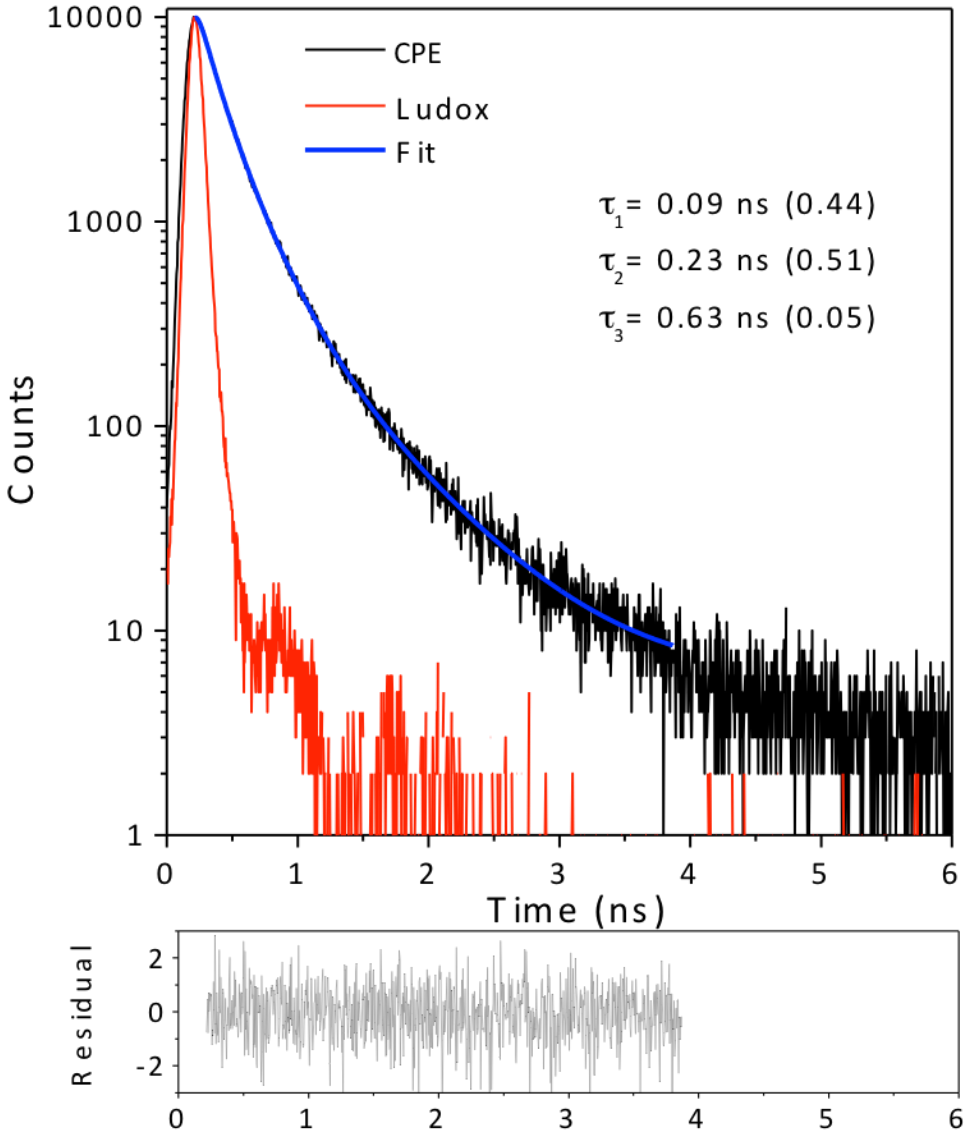

Fig. S4 Fluorescence lifetime decay of **CPE** (λ_{ex} = 405 nm) in H_2O detected at 464 nm. [**CPE**] = 5.0 μM in polymer repeat unit (PRU).

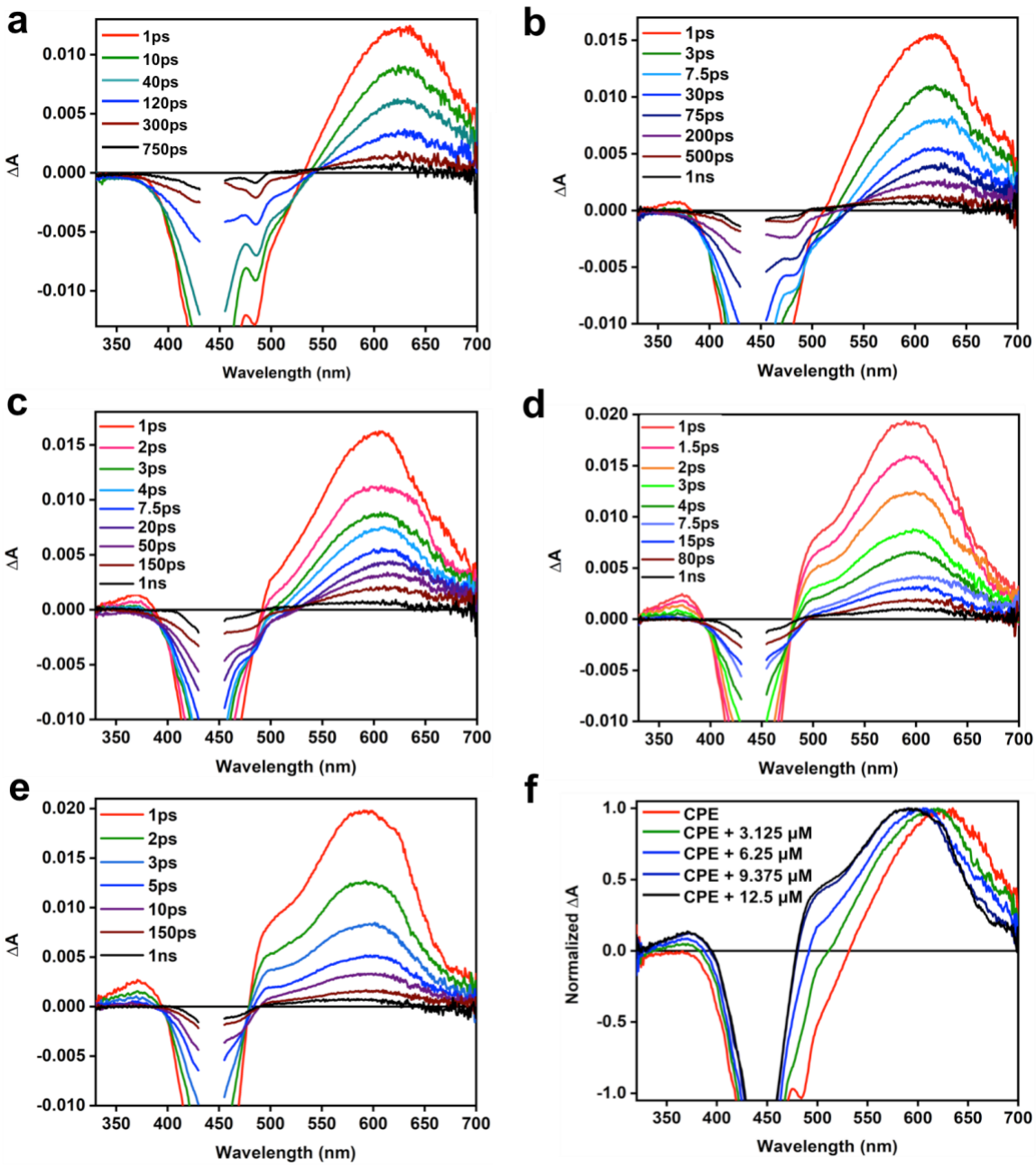

Fig. S5 Picosecond TA spectra of **CPE** in the presence of (a) 0 μM, (b) 3.125 μM, (c) 6.25 μM, (d) 9.375 μM and (e) 12.5 μM. and (f) 0 μM to 12.5 μM $\mathbf{MV}^{2+}$ at 10 ps delay time in air-saturated H_2O following 440 nm laser excitation pulse (100 fs pulse width, 100 nJ/pulse). [**CPE**] = 12.5 μM (PRU).

Table S1. Picosecond TA kinetics data for **CPE**, **CPE/MV^{2+}** and **CPE/ MV^{2+}/CB7** in water. The relative amplitudes are in parenthesis.

	Lifetimes		
	τ_1	**τ_2**	**τ_3**
CPE (12.5 µM)	3.0 ± 0.2 ps (0.41)	49 ± 6 ps (0.30)	264 ± 24 ps (0.29)
CPE + 3.125 µM MV^{2+}	2.5 ± 0.1 ps (0.59)	116 ± 5 ps (0.25	Inf (0.04)
CPE + 6.25 µM MV^{2+}	2.0 ± 0.1 ps (0.74)	115 ± 5 ps (0.23)	Inf (0.03)
CPE + 9.375 µM MV^{2+}	2.0 ± 0.1 ps (0.87)	120 ± 5 ps (0.10)	Inf (0.03)
CPE + 12.5 µM MV^{2+}	2.0 ± 0.1 ps (0.89)	115 ± 10 ps (0.08)	Inf (0.03)
CPE + 12.5 µM MV^{2+} + 125 µM CB7	4.0 ± 0.2 ps (0.41)	60 ± 6 ps (0.30)	610 ± 60 ps (0.29)

Table S2. Picosecond transient absorption kinetics data for **CPE** and **CPE/NDI$_{2+}$** in water. The relative amplitudes are in parenthesis.

	Lifetimes		
	τ_1	**τ_2**	**τ_3**
Only CPE (12.5 µM)	3.0 ± 0.2 ps (0.41)	49 ± 6 ps (0.30)	264 ± 24 ps (0.29)
CPE + 12.5 µM NDI$_{2+}$	3.0 ± 0.3 ps	-	-

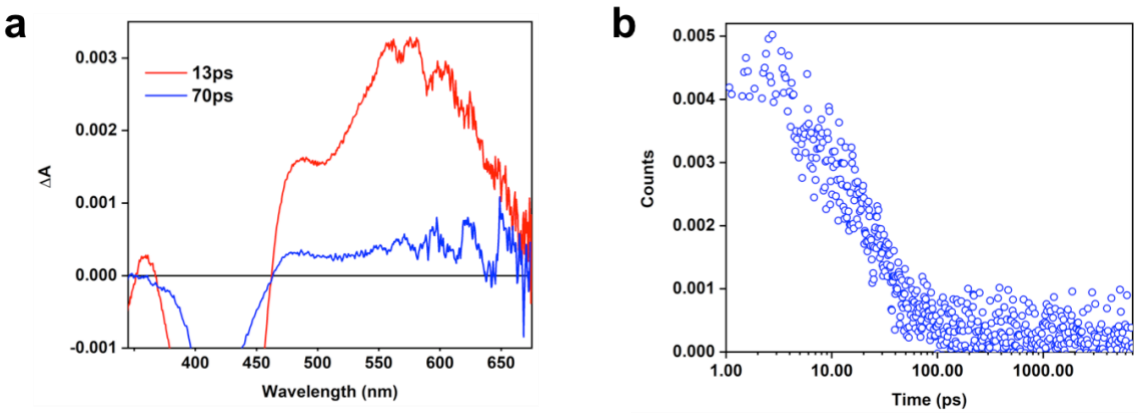

Fig. S6 (a) Picosecond TA spectra of **CPE** (12.5 µM, PRU) + 12.5 µM **NMI$_{+}$** in air-saturated H_2O at indicated delay times following 440 nm laser excitation pulse (100 fs pulse width, 100 nJ/pulse). (b) Kinetic decay trace of **CPE/NMI$_{+}$**.

Table S3. Picosecond TA kinetics data for **CPE** and **CPE/NMI+** in water. The relative amplitudes are in parenthesis.

CPE-Acceptor Complex	Lifetimes		
	τ_1	τ_2	τ_3
Only CPE (12.5 μM)	3.0 ± 0.2 ps (0.41)	49 ± 6 ps (0.30)	264 ± 24 ps (0.29)
CPE + 12.5 μM NMI+	35 ± 5 ps	-	-

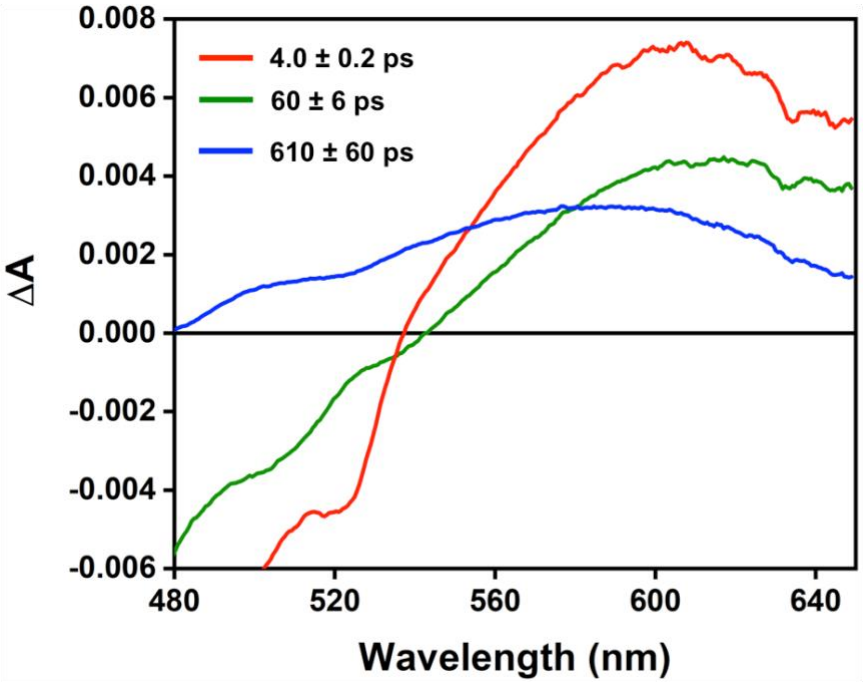

Fig. S7 Eigenspectra from global analysis of spectral-kinetic data for **CPE/MV2+/CB7** mixture (**CPE** = 12.5 μM, **MV2+** = 12.5 μM, **CB7** = 125 μM) in H_2O (440 nm excitation,100 fs pulse width, 100 nJ/pulse).

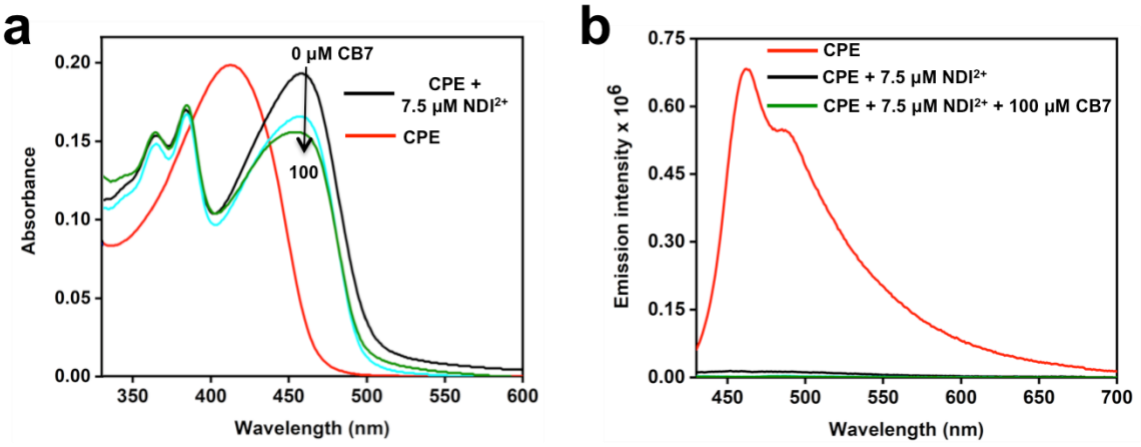

Fig. S8 (a) Absorption and (b) fluorescence (λ_{ex} = 410 nm) spectra of **CPE/NDI**$_{2+}$ in water with varying concentrations of **CB7** as indicated in the figure. **CPE** = 5 μM (PRU).

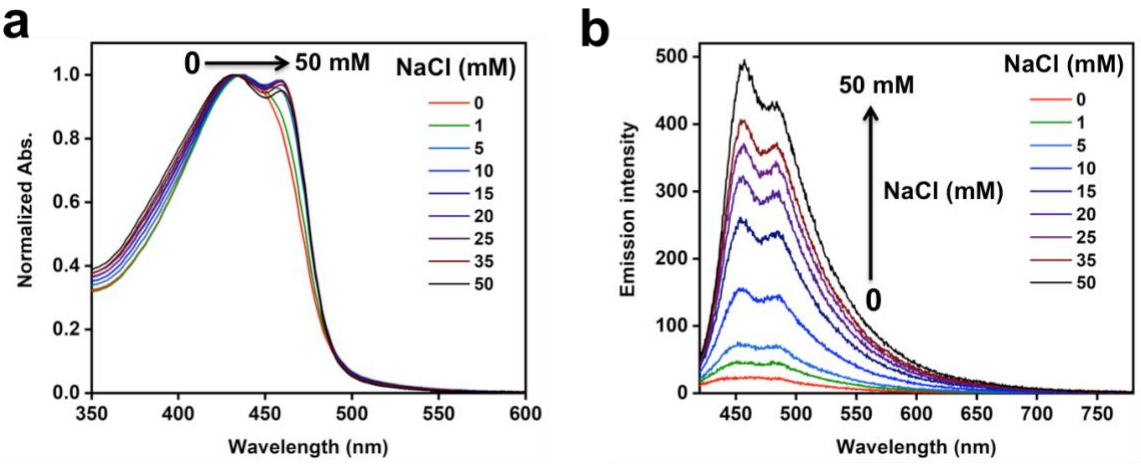

Fig. S9 (a) Normalized absorption and (b) fluorescence (λ_{ex} = 410 nm) spectra of **CPE** (5 μM, PRU) + **MV** (7.5 μM) in water with varying concentrations of **NaCl** as indicated in the figure.

References.

1. P. Jagadesan, K. S. Schanze, Poly(phenylene ethynylene) Conjugated Polyelectrolytes Synthesized via Chain-Growth Polymerization, *Macromolecules*, 2019, **52**, 10, 3845-3851.

2. C. J. Zhong, W. S. V. Kwan, L. L. Miller, Self-Assembly of Delocalized π-Stacks in Solution. Assessment of Structural Effects, *Chem. Mater.*, 1992,**4**, 1423-1428.