Electronic Supplementary Information (ESI)

Optically responsive switchable ionic liquid for internally-referenced fluorescence monitoring and visual determination of carbon dioxide

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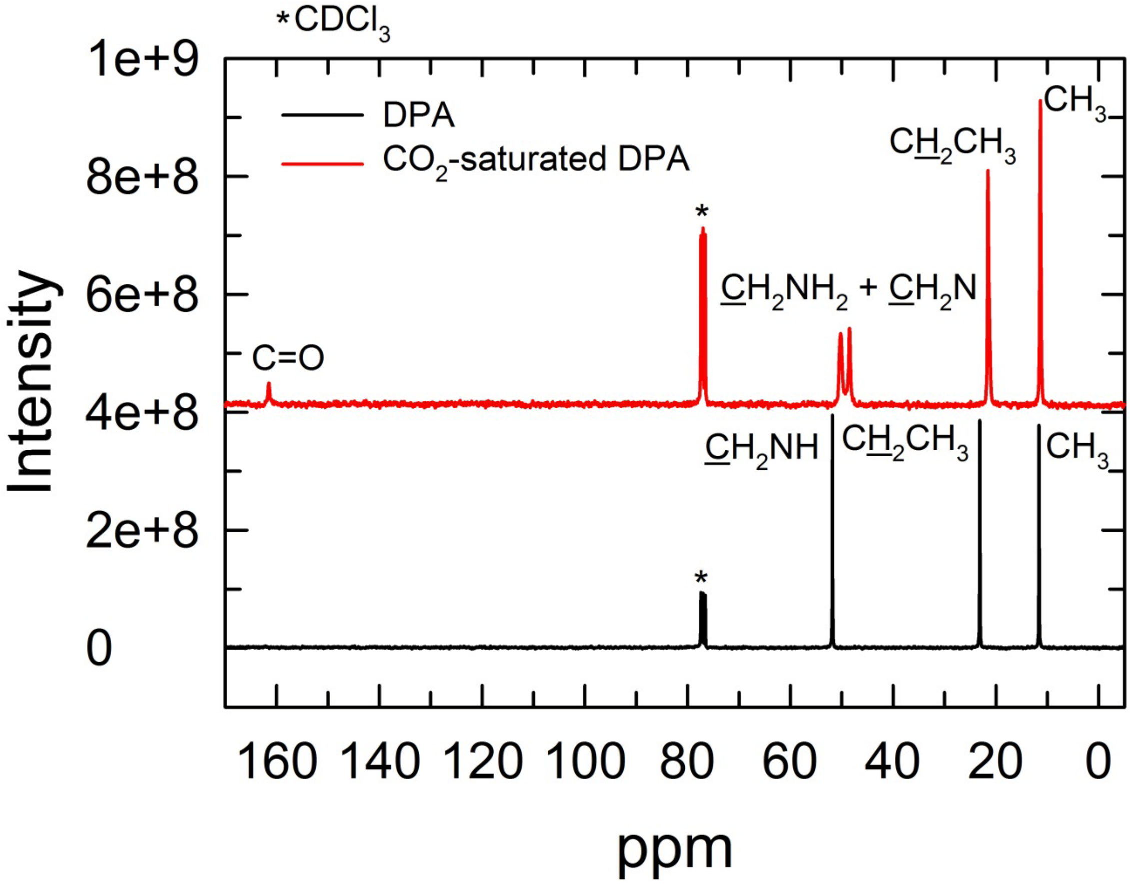

Fig. S1 ^{13}C NMR spectra of di-*n*-propylamine (DPA) (black) and CO$_2$-saturated DPA (red), each dissolved in CDCl$_3$ at ambient conditions. * denotes the residual solvent peak.

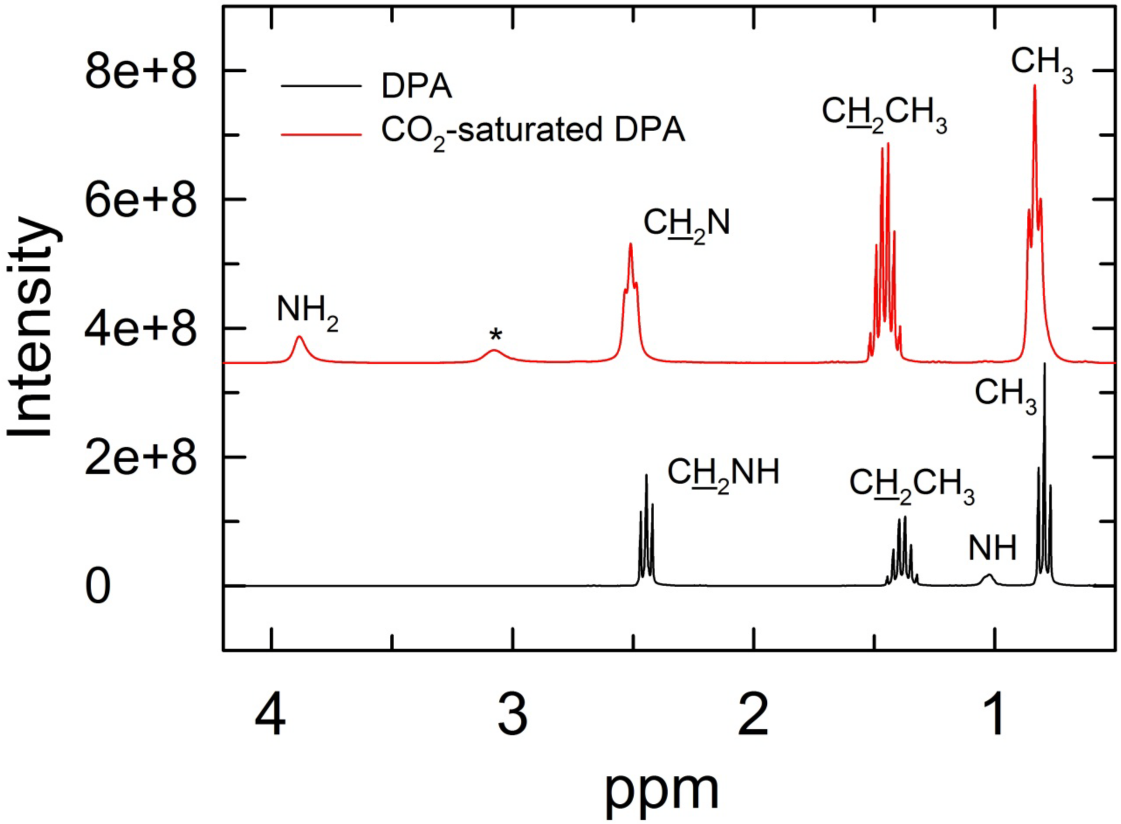

Fig. S2 ^{1}H NMR spectra of DPA (black) and the CO_2-saturated DPA mixture (red), both dissolved in $CDCl_3$. * denotes a peak tentatively assigned to the zwitterionic form $\underline{H}N^+$(*n*-propyl)$_2COO^-$.

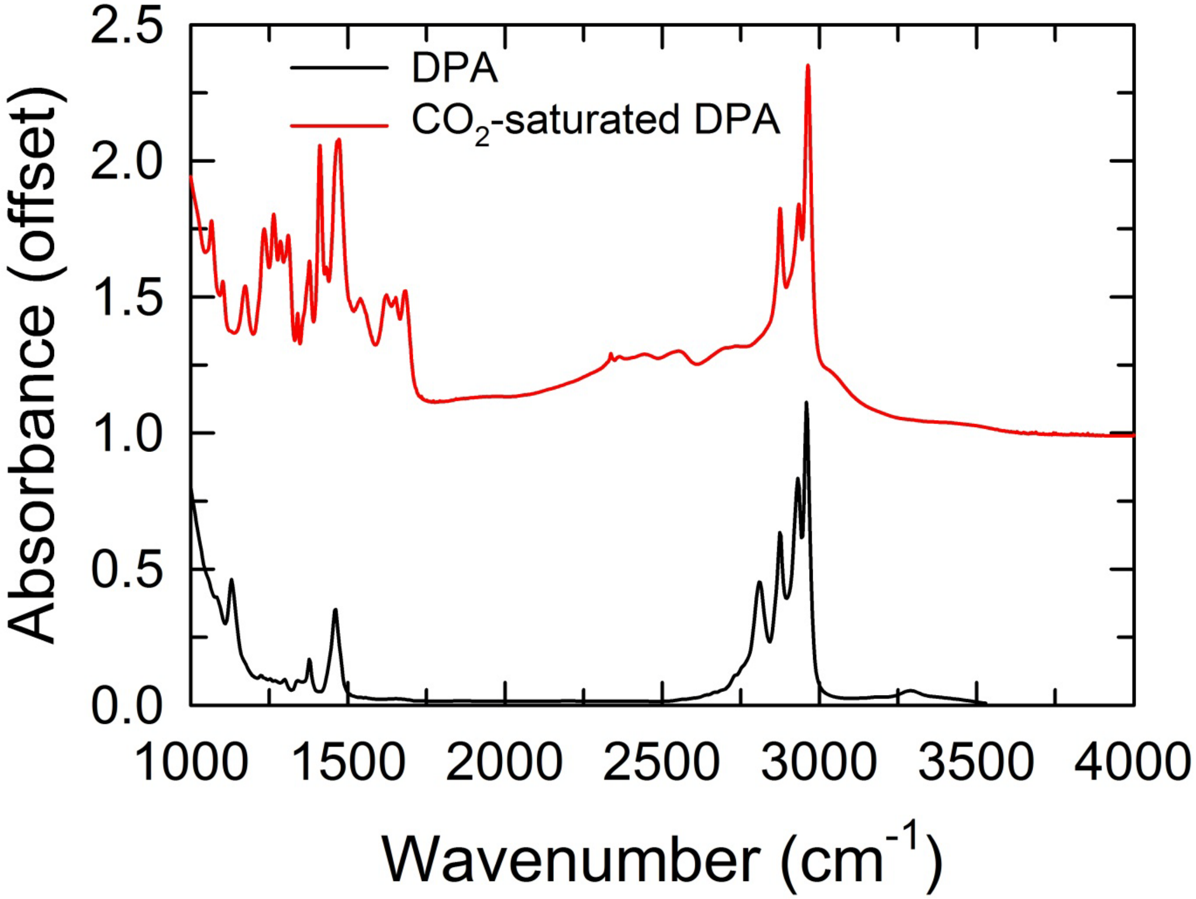

Fig. S3 FTIR absorbance spectra of DPA (black) and the corresponding CO_2-saturated DPA mixture (red).

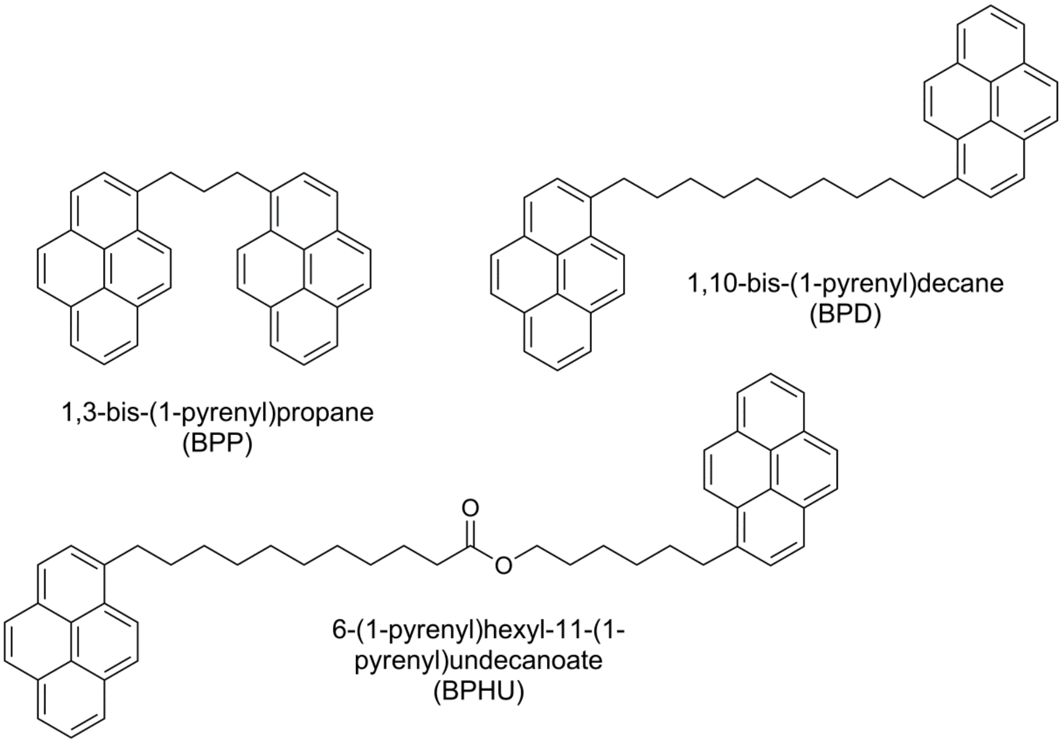

Fig. S4 Structures of the fluorescent probes BPP, BPD, and BPHU.

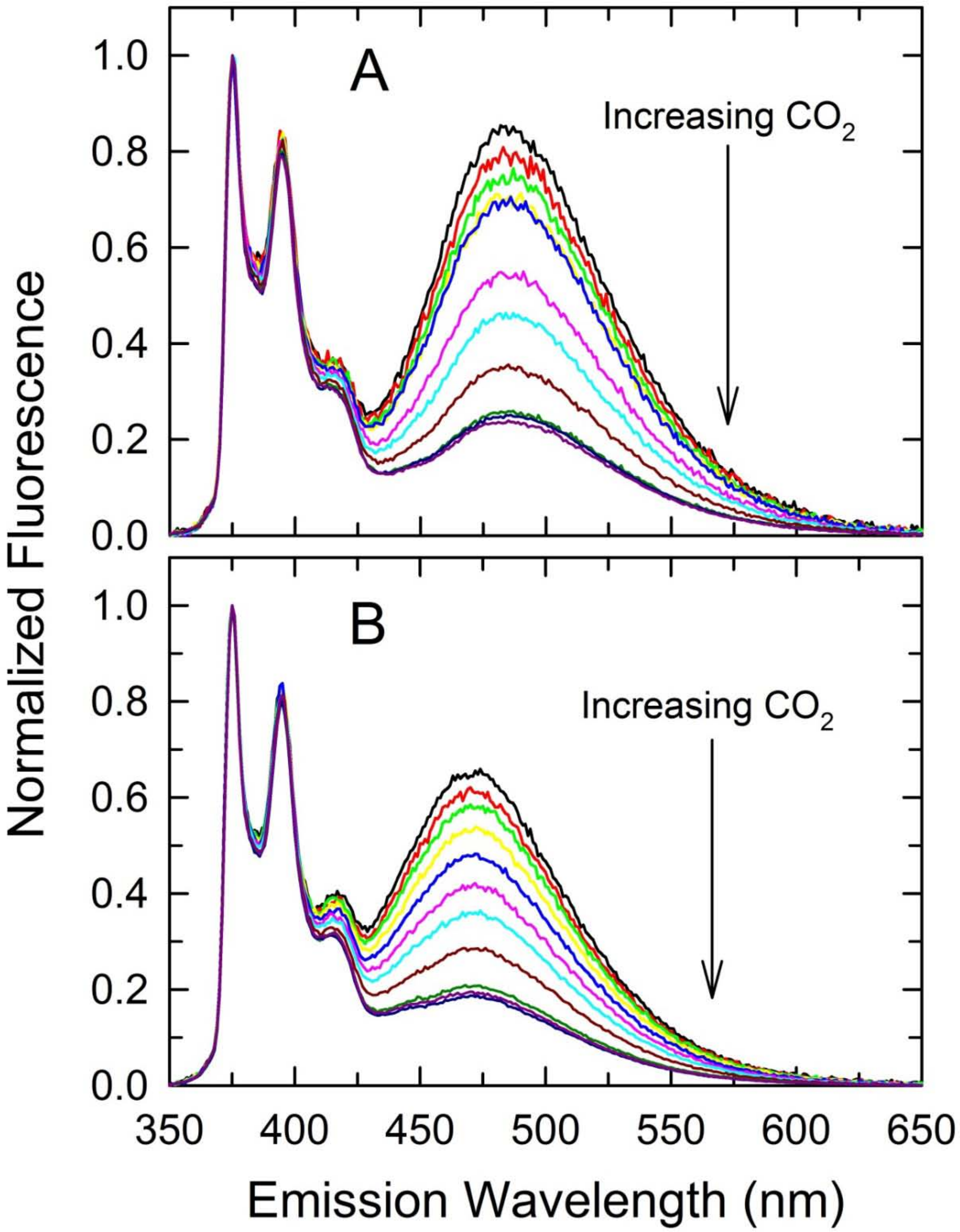

Fig. S5 Normalized fluorescence emission spectra of BPP (10 μM, panel A) and BPD (10 μM, panel B) dissolved in DPA as a function of captured CO_2 under ambient conditions (λ_{ex} = 337 nm, excitation and emission slit widths are both 5 nm).

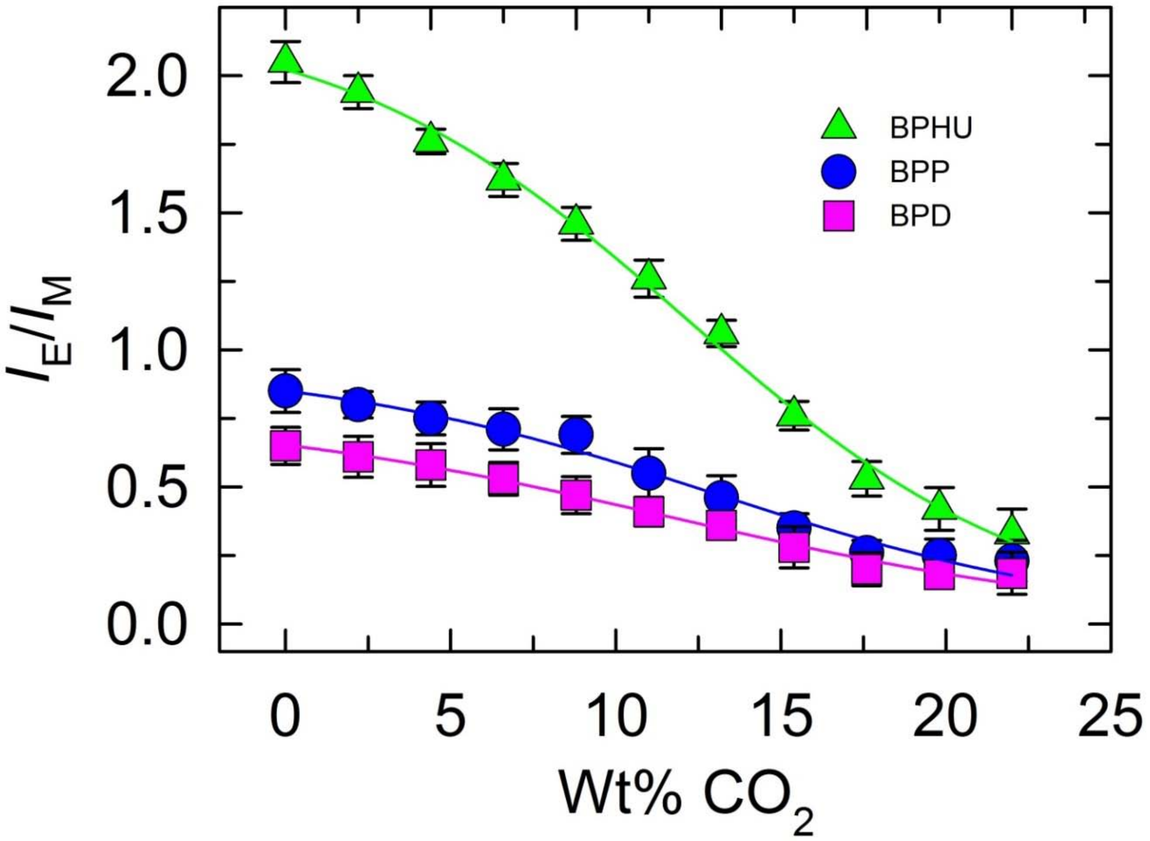

Fig. S6 Variation in the excimer-to-monomer emission intensity ratio (I_E/I_M) with wt% CO_2 within CO_2-added DPA solution for BPHU, BPP, and BPD at ambient temperature. Fits of the experimental data to a 3-parameter sigmoidal expression of the form $I_E/I_M = a/[1+\exp\{-(\mathrm{wt\%CO_2} - x_0)/b\}]$ are shown by solid curves.

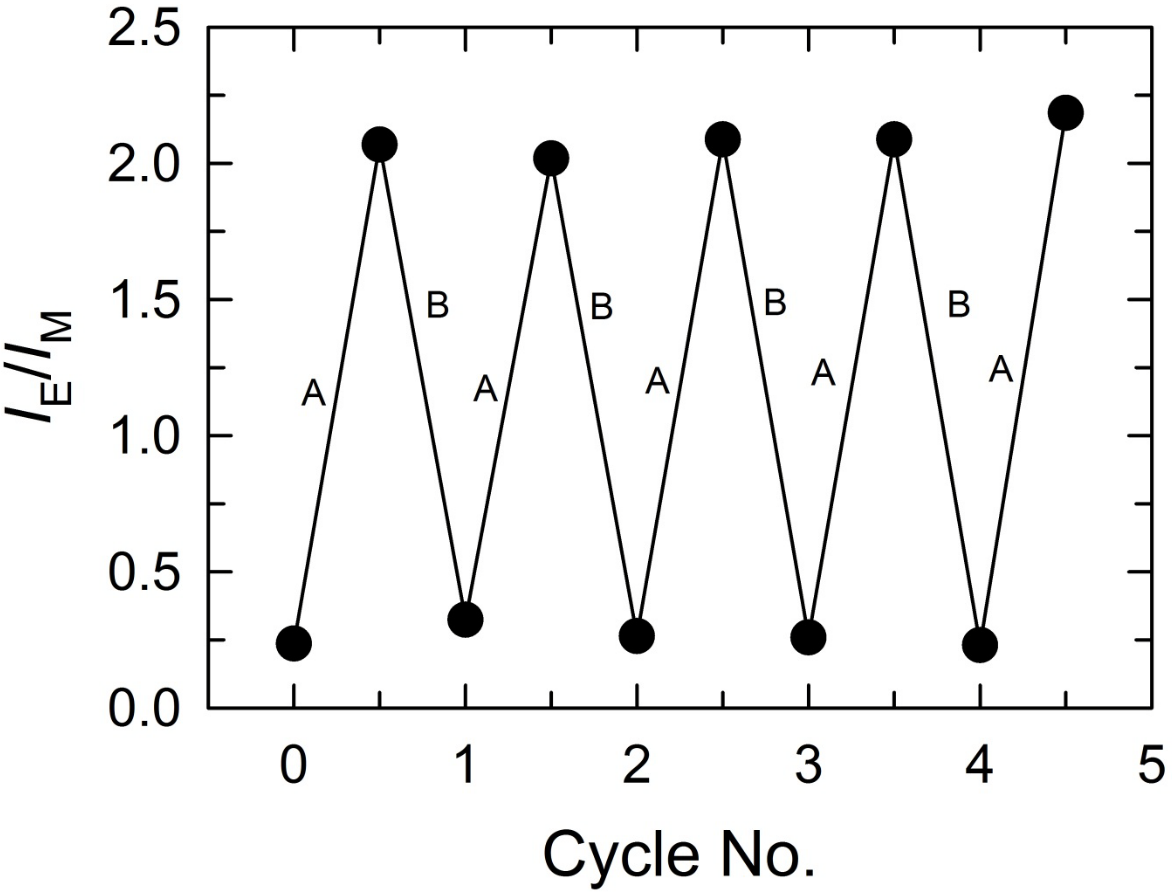

Fig. S7 Variation in the excimer-to-monomer ratio (I_E/I_M) for BPHU in DPA with consecutive heating/CO_2-addition cycles. Leg A involves heating of a CO_2-containing DPA mixture at 100 °C for 8 min whilst stirring at 150 rpm. B entails CO_2 addition at a flow of 50 mL min^{-1} into 10 g of DPA for 30 min, again with stirring. The typical imprecision in I_E/I_M is less than 0.1.

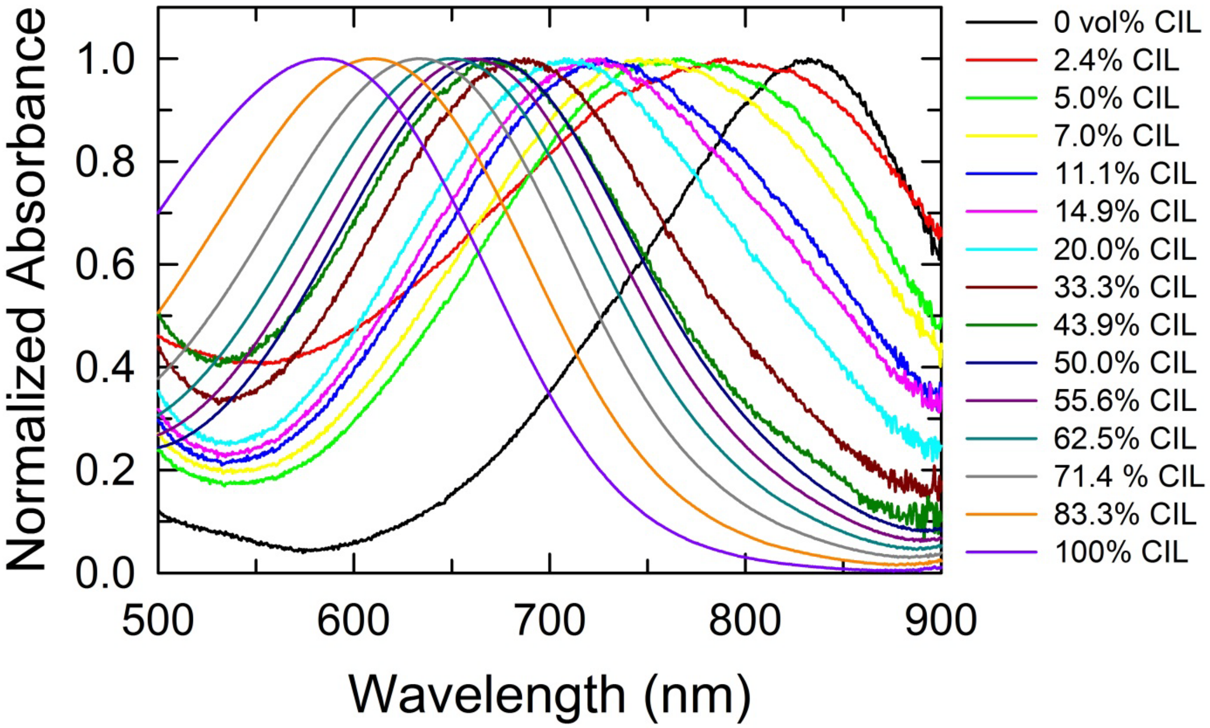

Fig. S8 Normalized absorbance spectra of betaine dye 30 (Reichardt's dye) dissolved at 100 μM in DPA as a function of conversion to the carbamate ionic liquid (CIL) at ambient temperature.

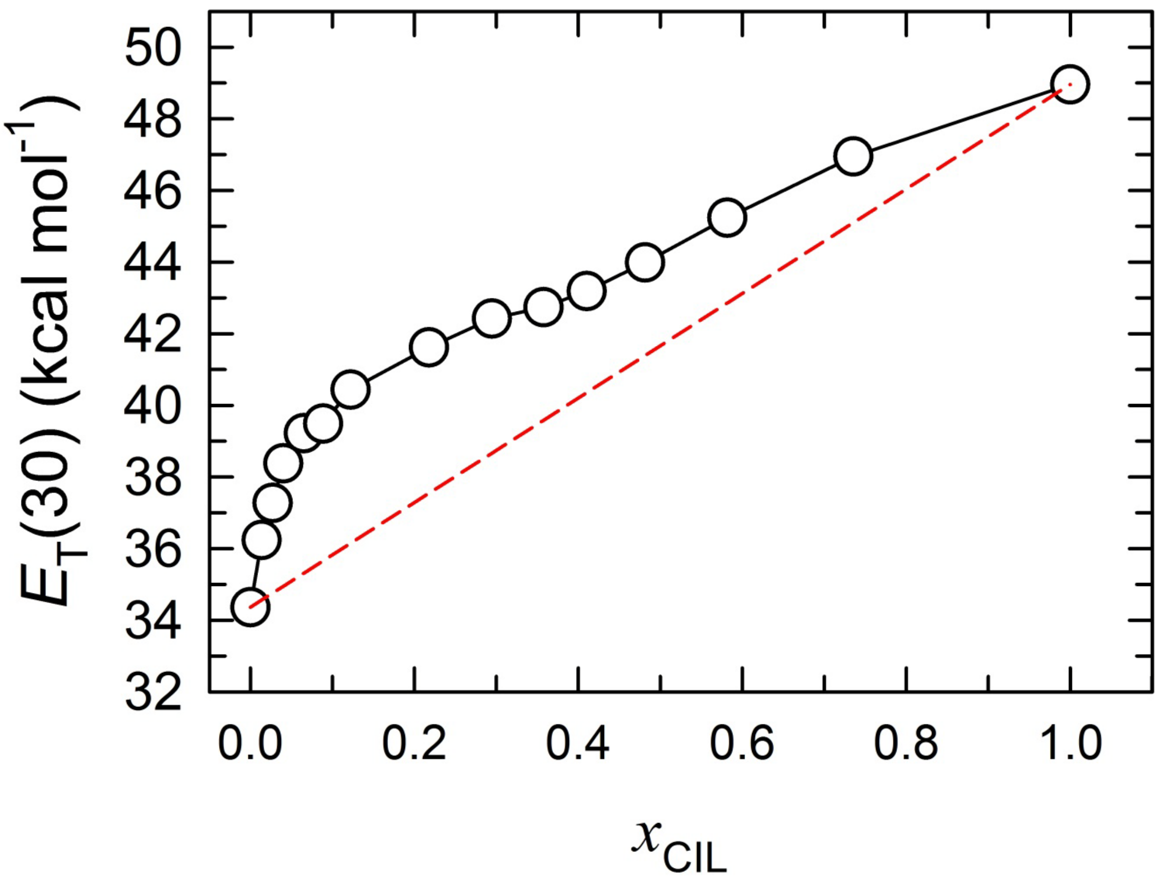

Fig. S9 $E_T(30)$ values determined from the wavelength of maximal absorbance for Reichardt's dye dissolved in DPA as a function of CIL mole fraction in the mixture under ambient conditions (symbols). The dashed line indicates the predicted response; *i.e.*, the ideal, mole fraction-weighted response. The uncertainty in $E_T(30)$ is better than 0.5 kcal mol^{-1}.

Calculation of Kamlet–Taft Empirical Solvatochromic Parameters.

Dipolarity/polarizability (π*) was estimated using the following expression:

$$\pi^* = 8.649 - 0.314\bar{\nu}_{DENA}$$

where $\bar{\nu}_{DENA}$ is the wavelength of absorbance maximum in kK (1 kK = 1000 cm^{-1}) for *N*,*N*-diethyl-4-nitroaniline (DENA). Hydrogen-bond accepting (HBA) basicity (β) was calculated based on the following expression using the wavelength of maximal absorbance ($\bar{\nu}_{NA}$ in kK units) of 4-nitroaniline:

$$\beta = -0.357\bar{\nu}_{NA} - 1.176\pi^* + 11.12$$

and hydrogen-bond donating (HBD) acidity (α) was calculated from:

$$\alpha = \left[\frac{E_T(30) - 14.6(\pi^* - 0.23\delta) - 30.31}{16.5}\right]$$

where $E_T(30)$ is obtained from the betaine dye 30 charge-transfer (CT) absorbance maximum and δ is a polarizability correction term. For non-aromatic and non-chlorinated solvents, where δ = 0, a condensed form of the above equation emerges:

$$\alpha = \left[\frac{E_T(30) - 14.6\pi^* - 30.31}{16.5}\right]$$