Photophysics of *N,N*-Dimethyl-3-(1-indolyl)propan-1-ammonium Chloride and Related Derivatives

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Materials Used:

Sodium sulfate anhydrous (Fisher, 99.9%), chloroform (Sigma Aldrich, 99.8%), diethyl ether anhydrous (Sigma Aldrich, $\geq$ 99%), acetonitrile HPLC Grade (EMD, 99.99%), chloroform-*d* (Cambridge Isotope Laboratories, Inc., 99.9%), 12M hydrochloric acid (Macron, 99%), indole (Sigma Aldrich, > 99%), 3-dimethylamino-1-propyl chloride hydrochloride (Sigma Aldrich, 96%), iodomethane (Sigma Aldrich, 99%), 18M sulfuric acid (Baker, 98%), and ethyl acetate (Sigma Aldrich, > 99.7%) were used as received. Tetrahydrofuran (anhydrous, Sigma Aldrich, 99.9%) and 1,4-dioxane anhydrous (Sigma Aldrich, 99.8%) were dried and purified through distillation over sodium and benzophenone (Sigma Aldrich, 99%). Dichloromethane (Fisher, 99.9%) was dried and purified by distillation over calcium hydride.

Synthesis of InCl and MeInCl:

Synthesis of N,N-Dimethyl-3-(1-indolyl)propan-1-ammonium Chloride (InCl)

A suspension of 3.8 g (160 mmol) NaH in 10 mL anhydrous THF was cooled to 0 °C. A solution of 3.0 g (26 mmol) indole in 10 mL anhydrous THF was added to it and it was stirred for 5 min under N_2. 4.2 g (27 mmol) 3-dimethylamino-1-propylchloride hydrochloride, suspended in 20 mL anhydrous THF, was added to the stirred suspension under N_2. The suspension was warmed to room temperature and then refluxed for 95 h. The conversion of indole into *N,N*-dimethyl-3-(1-indolyl)propylamine was monitored by HPLC. At 95% conversion, the reaction mixture was cooled to room temperature and excess base was deactivated through the dropwise addition of distilled water. The aqueous phase was extracted with ethyl acetate (3x50 mL). The organic layers were combined and washed with distilled water (3x50 mL) and then dried over anhydrous sodium sulfate. The dried organic layer was condensed by vacuum distillation at 25 torr. Approximately 0.50 g of a residue, a yellow oil, was dissolved in 30 mL of diethyl ether. Anhydrous HCl gas was prepared by the slow addition of concentrated HCl into concentrated H_2SO_4. HCl gas was passed through a $CaCl_2$ drying tube and bubbled into the ether solution. A beige precipitate rapidly formed. Crude solid (2.29 g) was filtered and dried. The compound was recrystallized three times from ethanol to give 1.48 g (24%) *N,N*-dimethyl-3-(1-indolyl)propan-1-ammonium chloride (InCl), mp 145 – 148 °C, and > 99.9% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.45 (2H, m, $CH_2\text{-}C\underline{H_2}\text{-}CH_2\text{-}NH(CH_3)_2$), 2.68 (6H, d, $N(C\underline{H_3})_2$), 2.81 (2H, m, $CH_2\text{-}CH_2\text{-}C\underline{H_2}\text{-}N(CH_3)_2$), 4.36 (2H, m, $C\underline{H_2}\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2$), 6.52 (1H, m, ArH), 7.13 (1H, m, ArH), 7.20 (2H, m, ArH), 7.32 (1H, m, ArH), 7.62 (1H, m, ArH), 12.80 (1H, s, $N\underline{H(}CH_3)_2$. Elemental analysis calculated for $C_{19}H_{20}N_1Cl$: C, 64.9; H, 8.6; N. 11.6. Found: C, 64.7; H, 8.8; N, 11.6.

Synthesis of N,N,N-Trimethyl-3-(1-indolyl)propan-1-ammonium Iodide (MeInI)

A suspension of 0.38 g (1.6 mmol) *N,N*-dimethyl-3-(1-indolyl)propan-1-ammonium chloride in 10 mL diethyl ether and 10 mL 3M aqueous NaOH was stirred for 30 min under flowing N_2 at room temperature. The aqueous layer was extracted 3x20 mL diethyl ether. The organic layers were combined and washed 3x20 mL with distilled water and dried over sodium sulfate. The dried organic layer was condensed using vacuum distillation at 25 torr. Approximately 300 mg of a yellow oil was dissolved in 25 mL acetonitrile and stirred under flowing N_2. Methyliodide (0.20 mL, 3.2 mmol) was added to the solution and the resulting mixture was stirred at room temperature under a static N_2 atmosphere at room temperature for 48 h. The solvent was removed with vacuum distillation at 25 torr to give 0.42 g (78%) *N,N,N*-trimethyl-3-(1-indolyl)propan-1-ammonium iodide (MeInI), mp 41 – 44 °C, and > 99.4% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.39 (2H, m, CH_2-$C\underline{H_2}$-CH_2-$N(CH_3)_3$), 3.28 (9H, d, $N(C\underline{H_3})_3$), 3.71 (2H, m, CH_2-CH_2-$C\underline{H_2}$-$N(CH_3)_2$), 4.42 (2H, m, $C\underline{H_2}$-CH_2-CH_2-$N(CH_3)_2$), 6.53 (1H, m, ArH), 7.16 (1H, m, ArH), 7.20 (2H, m, ArH), 7.43 (1H, m, ArH), 7.63 (1H, m, ArH).

Synthesis of N,N,N-Trimethyl-3-(1-indolyl)propan-1-ammonium Chloride (MeInCl)

N,N,N-Trimethyl-3-(1-indolyl)propan-1-ammonium chloride was prepared through counterion substitution of MeInI using a 24 cm x 4 cm Dowex 22 ion exchange column that was washed first with distilled water and then activated with 3M HCl. The activated column was washed again with water and then with methanol. MeInI (200 mg) was dissolved in methanol and eluted through the column. The solvent was removed by vacuum distillation at 25 torr to give 80 mg (55%) of *N,N,N*-trimethyl-3-(1-indolyl)propan-1-ammonium chloride (MeInCl) of > 99.8%

purity by HPLC. Plasma-assisted chemical ionization mass spectroscopy indicated 99.4% counterion substitution. δH ($CDCl_3$, 400 MHz), 2.38 (2H, m, CH_2-$C\underline{H_2}$-CH_2-$N(CH_3)_3$), 3.30 (9H, d, $N(C\underline{H_3})_3$), 3.71 (2H, m, CH_2-CH_2-$C\underline{H_2}$-$N(CH_3)_2$), 4.39 (2H, m, $C\underline{H_2}$-CH_2-CH_2-$N(CH_3)_2$), 6.52 (1H, m, ArH), 7.15 (3H, m, ArH), 7.37 (1H, m, ArH), 7.63 (1H, m, ArH).

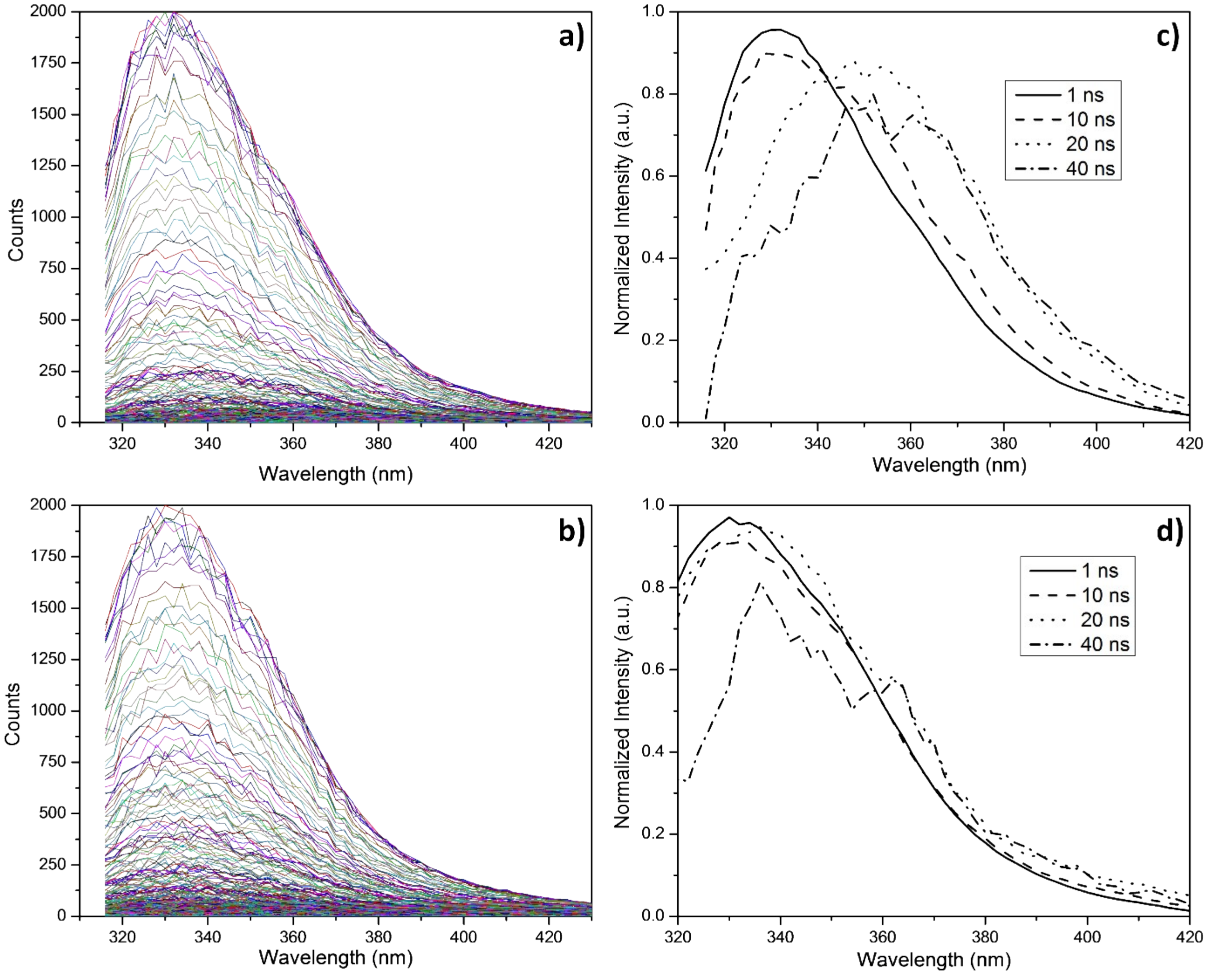

Figure S1: Time-resolved emission spectra (λ_{ex} = 295 nm) of 10^{-4} M MeI in a) 1,4-dioxane and b) acetonitrile 293 K. TRES spectra collected at delay times of 1, 10, 20, and 40 ns were normalized and smoothed using the adjacent-average method for 10^{-4} M MeI in c) 1,4-dioxane and d) acetonitrile.