Proton-Coupled Charge-Transfer Reactions and Photoacidity of *N,N*-Dimethyl-3-arylpropan-1-ammonium Chloride Salts

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Supporting Information

Materials:

Sodium sulfate anhydrous (Fisher, 99.9%), chloroform (Sigma Aldrich, 99.8%), diethyl ether anhydrous (Sigma Aldrich, $\geq$ 99%), acetonitrile HPLC Grade (EMD, 99.99%), lithium aluminum hydride (Sigma Aldrich, 95%), 9-anthraldehyde (Sigma Aldrich, 97%), chlorobenzene (Sigma Aldrich, 99%), glacial acetic acid (Baker, 99.9%), dimethylsulfoxide-d_6 (D, 99.9%; Cambridge Isotope Laboratories, Inc.), 2-naphthaldehyde (Sigma Aldrich, 98%), 9-anthraldehyde (Sigma Aldrich, 98%), malonic acid (Alfa Aesar, $\geq$ 99.5%), pyridine (Fisher, 98%), piperidine (Sigma Aldrich, 99%), sodium sulfate (Fisher, 99.2%), 10% palladium on carbon (Sigma Aldrich), compressed hydrogen gas (GTS-Welco), *N,N*-dimethylformamide (Alfa Aesar, 99.8%), thionyl chloride (Sigma Aldrich, ≥ 99.9%), chloroform-*d* (Cambridge Isotope Laboratories, Inc., 99.9%), 12M hydrochloric acid (Macron, 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. Dichloromethane (Fisher, 99.9%) was dried and purified by distillation over calcium hydride.

Instrumentation:

^{1}H-NMR spectra were recorded using a Varian 400 MHz NMR spectrometer and analyzed using MestReNova software (v. 5.2.4-3924). HPLC experiments were performed using an Agilent Technologies 1220 Infinity LC with a Waters μBondpack C18 column (300 x 3.0 mm, 10 μm particle size). A ratio of 80:20 (v:v) methanol:ethyl acetate was used as the mobile phase to elute each of ArCl at a flow rate of 1.0 mL/min. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer using acetanilide as a calibration standard.

Synthesis:

Synthesis of N,N-dimethyl-3-arylpropan-1-amines (ArA)

N,N-dimethyl-3-arylpropan-1-amine (ArA) was prepared by suspending 20 mg of the corresponding ArS in 10 mL diethyl ether and stirring with 20 mL 30% NaOH (aqueous) under flowing N_2 for 30 min. ArA was extracted with diethyl ether and washed with water to remove excess base. The solutions of ArA were dried over Na_2SO_4 and concentrated on a rotary evaporator. HPLC analysis indicated greater than 99.5% purity for each ArA.

Synthesis of N,N-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride (PyCl)

The synthesis of *N,N*-dimethyl-3-(1-pyrenyl)propan-1-ammonium chloride (PyCl) was accomplished using a previously established synthetic route.[9]

Synthesis of N,N-dimethyl-3-(9-anthryl)propan-1-ammonium chloride (AnCl)

0.60 g (2.2 mmol) *N,N*-dimethyl-3-(9-anthryl)propan-1-amide was dissolved in 10 mL anhydrous THF and added dropwise to a stirred suspension of 0.39 g (10.2 mmol) $LiAlH_4$ in 20 mL anhydrous THF under flowing N_2 in a three-neck round-bottom flask. The reaction mixture was refluxed under flowing N_2 for 26 h. The suspension was cooled to room temperature and 5 mL of acetone was added under N_2. 30 mL diethyl ether was then added. Finally, 2 mL deionized water was added dropwise. The lithium salts were filtered and the organic solution was dried over Na_2SO_4 and condensed by vacuum distillation at 25 torr. *N,N*-dimethyl-3-(9-

anthryl)propan-1-amine was dissolved in 50 mL diethyl ether and stirred. Gaseous HCl was formed by adding concentrated hydrochloric acid dropwise to stirred concentrated sulfuric acid. The gas was passed through anhydrous calcium sulfate and bubbled through the solution of *N,N*-dimethyl-3-(9-anthryl)propan-1-amine for 20 min to give a brown precipitate that was filtered and recrystallized three times in dichloromethane/diethyl ether to give 0.38 g (59%) of *N,N*-dimethyl-3-(9-anthryl)propan-1-ammonium chloride (AnCl), mp 189 – 190 °C, >99.8% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.36 (2H, m, CH_2-$C\underline{H_2}$-CH_2-$NH(CH_3)_2$), 2.63 (6H, s, $N(C\underline{H_3})_2$), 3.03 (2H, m, CH_2-CH_2-$C\underline{H_2}$-$NH(CH_3)_2$), 3.71 (2H, m, $C\underline{H_2}$-CH_2-CH_2-$NH(CH_3)_2$), 7.43 (4H, m, ArH), 7.96 (2H, d, ArH), 8.14 (2H, d, ArH), 8.32 (1H, s, ArH), 12.49 (1H, s, $N\underline{H}$). Elemental analysis calculated for $C_{19}H_{22}N_1Cl$: C, 76.1; H, 7.4; N. 4.7. Found: C, 75.9; H, 7.4; N, 4.7.

Synthesis of N,N-dimethyl-3-(9-anthryl)propan-1-amide

0.22 g (0.88 mmol) 3-(9-Anthryl)propanoic acid was dissolved in 10 mL anhydrous DMF and stirred under flowing N_2 in a three-neck flask. The solution was cooled to 0 °C and 0.12 mL (1.7 mmol) thionyl chloride was added dropwise. The solution was warmed to 90 °C and the reaction was stirred for 22 h. The solution was cooled to room temperature and excess DMF and thionyl chloride were removed by vacuum distillation at 2 torr as the temperature was warmed from 20 to 55 °C. The crude reaction mixture was dissolved in 200 mL dichloromethane and washed with 100 mL deionized H_2O. The aqueous layer was extracted with 3x50 mL dichloromethane. The organic layers were combined and washed with 5x100 mL deionized water. The organic layer was dried over Na_2SO_4 and condensed with vacuum distillation at 25 torr to give 0.22 g (90%) of a red oil, *N,N*-dimethyl-3-(9-anthryl)propan-1-amide for a yield of 93%, >99.9% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.68 (3H, s, $NC\underline{H_3}$), 2.71 (2H, m, CH_2-$C\underline{H_2}$-$CON(CH_3)_2$), 2.90 (3H, s, $NC\underline{H_3}$), 3.93 (2H, m, $C\underline{H_2}$-CH_2-$CON(CH_3)_2$), 7.43 (4H, m, ArH), 7.94 (2H, d, ArH), 8.21 (2H, d, ArH), 8.30 (1H, s, ArH).

Synthesis of 3-(9-anthryl)propanoic acid

3.47 g (14.0 mmol) 3-(9-Anthryl)propenoic acid was added to a one-neck round-bottom flask with 0.35 g (0.32 mmol) 10% palladium on carbon and 15 mL dry DMF. The suspension was stirred in a flowing N_2 atmosphere for 30 min to displace O_2. A balloon of H_2 gas was affixed to the flask to commence hydrogenation at ~ 1 atm of H_2. The solution was stirred under H_2 for 48 h. The reaction was quenched by displacement of the H_2 with N_2. The suspension was filtered through celite to remove the catalyst. The filtrate was diluted with 100 mL ethyl acetate and washed 100 mL deionized water. The aqueous phase was extracted with 3x50 mL ethyl acetate. The organic layers were combined and washed with 5x100 mL deionized water. The organic layer was dried with $MgSO_4$. The solvent was removed by vacuum distillation at 25 torr and the crude product was recrystallized three times in ethanol to give 2.20 g (81%) of 3-(9-anthryl)propanoic, mp 189-190 °C, >95.0% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.85 (2H, m, CH_2-$C\underline{H_2}$-COOH), 3.99 (2H, m, $C\underline{H_2}$-CH_2-COOH), 7.52 (4H, m, ArH), 8.02 (2H, d, ArH), 8.26 (2H, d, ArH), 8.38 (1H, d, ArH).

Synthesis of 3-(9-anthryl)propenoic acid

10.00 g (48.49 mmol) 9-Anthraldehyde was added to an open round bottom flask with 7.02 g (67.5 mmol) malonic acid, 45 mL pyridine and 6 mL piperidine. The solution was heated in an oil bath at 100 – 110 °C for 4 h. Then, a condenser was added and the solution was refluxed for 2 h at 120 °C. 220 mL distilled water was added to quench the reaction. The solution was acidified to a pH of 3 with concentrated HCl. The orange oil solidified and was filtered and washed with distilled water. The solid was dried by vacuum suction and heated uncovered in a beaker from 170 – 185 °C. The crude product was recrystallized 5 times with 4% acetic acid in chlorobenzene to give 8.94 g (44%) of 3-(9-anthryl)propenoic acid, mp 235 – 237 °C, 98.5 % purity by HPLC. δH (DMSO-d_6, 400 MHz), 6.46 (1H, d, vinyl-CH), 7.71 (4H, m, ArH), 8.29 (4H, m, ArH), 8.61 (1H, d, vinyl-CH), 8.79 (1H, s, ArH), 12.88 (1H, s, COOH).

Synthesis of N,N-dimethyl-3-(2-naphthyl)propan-1-ammonium chloride (NapCl)

2.03 g (8.93 mmol) *N,N*-Dimethyl-3-(2-naphthyl)propan-1-amide was dissolved in 10 mL anhydrous THF and added dropwise to a stirred suspension of 1.90 g (31.3 mmol) $LiAlH_4$ in 20 mL anhydrous THF under flowing N_2 in a three-neck round-bottom flask. The reaction mixture was refluxed under flowing N_2 for 26 h. The suspension was cooled to room temperature and 5 mL of acetone was added under N_2. 30 mL diethyl ether was then added. Finally, 2 mL deionized water was added dropwise. The lithium salts were filtered and the organic solution was dried over Na_2SO_4 and condensed by vacuum distillation at 25 torr. *N,N*-dimethyl-3-(2-

naphthyl)propan-1-amine was dissolved in 50 mL diethyl ether and stirred. Gaseous HCl was formed by adding concentrated hydrochloric acid dropwise to stirred concentrated sulfuric acid. The gas was passed through anhydrous calcium sulfate and bubbled through the solution of *N,N*-dimethyl-3-(2-naphthyl)propan-1-amine, quickly forming a beige precipitate. 0.94 g of amorphous solid was recovered and recrystallized with dichloromethane and diethyl ether to give 0.62 g (28%) of *N,N*-dimethyl-3-(2-naphthyl)propan-1-ammonium chloride (NapCl), mp 175 – 176 °C, >99.9% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.28 (2H, m, CH_2-$C\underline{H_2}$-CH_2-$NH(CH_3)_2$), 2.73 (6H, d, $N(C\underline{H_3})_2$), 2.90 (4H, m, $C\underline{H_2}$-CH_2-$C\underline{H_2}$-$N(CH_3)_2$), 7.29 (2H, m, ArH), 7.45 (2H, m, ArH), 7.61 (1H, m, ArH), 7.77 (2H, m, ArH), 12.67 (1H, s, $N\underline{H(}CH_3)_2$. Elemental analysis calculated for $C_{19}H_{20}N_1Cl$: C, 72.1; H, 8.1; N. 5.6. Found: C, 72.0; H, 8.4; N, 5.7.

Synthesis of N,N-dimethyl-3-(2-naphthyl)propan-1-amide

1.82 g (9.08 mmol) 3-(2-Naphthyl)propanoic acid was dissolved in 10 mL anhydrous DMF and stirred under flowing N_2 in a three-neck flask. The solution was cooled to 0 °C and 1.37 mL (18.9 mmol) thionyl chloride was added dropwise. The solution was warmed to 90 °C and the reaction was stirred for 22 h. The solution was cooled to room temperature and excess DMF and thionyl chloride were removed by vacuum distillation at 2 torr as the temperature was warmed from 20 to 55 °C. The crude reaction mixture was dissolved in 200 mL dichloromethane and washed with 100 mL deionized H_2O. The aqueous layer was extracted with 3x50 mL dichloromethane. The organic layers were combined and washed with 5x100 mL deionized water. The organic layer was dried over Na_2SO_4 and condensed with vacuum distillation at 25 torr to give 2.03 g (98%) of a red oil (*N,N*-dimethyl-3-(2-naphthyl)propan-1-amide), >99.9% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.71 (2H, d, CH_2-$C\underline{H_2}$-$CON(CH_3)_2$), 2.95, 6H, d, $N(C\underline{H_3})_2$), 3.14 (2H, d, $C\underline{H_2}$-CH_2-$CON(CH_3)_2$), 7.39 (3H, m, ArH), 7.66 (1H, s, ArH), 7.79 (3H, m, ArH).

Synthesis of 3-(2-naphthyl)propanoic acid

2.80 g (14.2 mmol) 3-(2-Naphthyl)propenoic acid was added to a one-neck round-bottom flask with 0.78 g 10% Pd/C and 30 mL anhydrous DMF. The suspension was stirred in a flowing N_2 atmosphere for 30 min to displace O_2. A balloon of H_2 gas was affixed to the flask to commence hydrogenation at ~ 1 atm of H_2. The solution was stirred under H_2 for 48 h. The reaction was quenched by displacement of the H_2 with N_2. The suspension was filtered through celite to remove the catalyst. The filtrate was diluted with 100 mL ethyl acetate and washed 100 mL deionized water. The aqueous phase was extracted with 3x50 mL ethyl acetate. The organic layers were combined and washed with 5x100 mL deionized water. The organic layer was dried with $MgSO_4$ and condensed through vacuum distillation at 25 torr. 3.17 g pale yellow solid was recovered. Recrystallization in acetone and water gave 1.82 g (64%) of 3-(2-naphthyl)propanoic acid, mp 134 – 135 °C, >98.5% purity by HPLC. δH ($CDCl_3$, 400 MHz), 2.74 (2H, d, CH_2-$C\underline{H_2}$-COOH), 3.08 (2H, m, ArH), 7.30 (1H, m, CH_2-$C\underline{H_2}$-COOH), 7.38 (2H, m, ArH), 7.61 (1H, s, ArH), 7.75 (3H, m, ArH).

Synthesis of 3-(2-naphthyl)propenoic acid

3.33 g (21.3 mmol) 2-Naphthaldehyde was added to a single-neck round bottom flask with 2.45 g (23.6 mmol) malonic acid, 1.2 mL (12 mmol) piperidine, and 50 mL pyridine. A reflux condenser was affixed to the round-bottom flask and the solution was stirred and refluxed for 3 h under atmospheric conditions. The solution was cooled to room temperature and diluted by the addition of 100 mL of ethyl acetate. The solution was then washed with 3x50 mL 1N HCl. The aqueous layer was extracted with 3x50 mL ethyl acetate. The organic layers were combined and washed 3x50 mL with deionized H_2O. The organic layer was dried over $MgSO_4$ and condensed on a rotary evaporator to give 4.05 g yellow solid. The solid was recrystallized in ethanol to give 2.80 g (67%) of 3-(2-naphthyl)propenoic acid, mp 208 – 210 °C, >95% purity by HPLC. δH ($CDCl_3$, 400 MHz), 6.54 (2H, d, vinyl-H), 7.49 (2H, m, ArH), 7.66 (2H, d, vinyl-H), 7.85 (5H, m, ArH).

Supporting Figures:

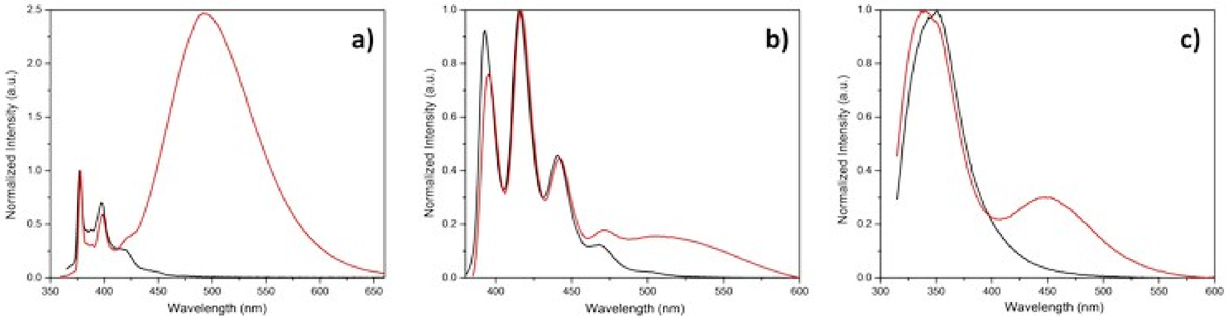

Figure S1: Normalized steady-state fluorescence spectra of 10^{-5} M a) PyCl (black) and PyA (red) ($\lambda_{excitation}$ = 344 nm) b) AnCl (black) and AnA (red) ($\lambda_{excitation}$ = 369 nm), and c) NapCl (black) and NapA (red) ($\lambda_{excitation}$ = 305 nm) at 293 K in dichloromethane.

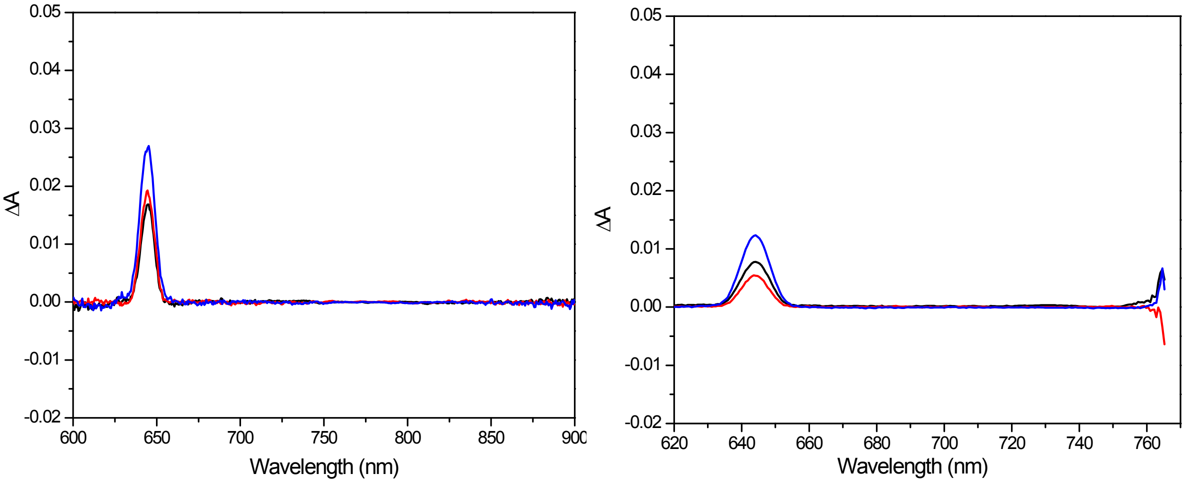

Figure S2: Transient absorption spectra of 10^{-5} M NapCl (*left*) and AnCl (*right*) in 1,4-dioxane (black), tetrahydrofuran (red), and acetonitrile (blue), collected at 1.4 ns after excitation (λ_{Ex} = 320 nm). The peaks at 640 nm are an artifact attributed to the second-order of the excitation pulse.

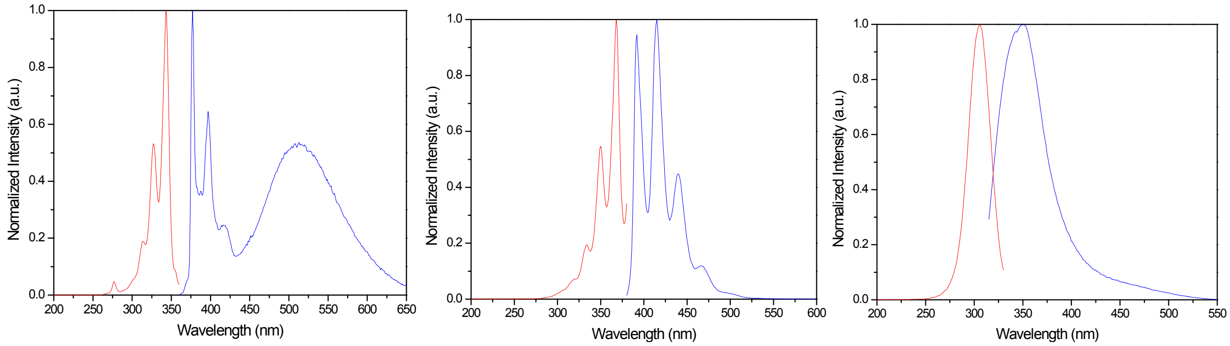

Figure S3: Normalized excitation (red) and emission (blue) spectra of a) 10^{-5} M PyCl ($\lambda_{excitation}$ = 344 nm, $\lambda_{emission}$ = 377 nm), b) 10^{-5} M AnCl ($\lambda_{excitation}$ = 369 nm, $\lambda_{emission}$ = 415 nm), and c) 10^{-5} M NapCl ($\lambda_{excitation}$ = 305 nm, $\lambda_{emission}$ = 350 nm) in THF at 292 K.

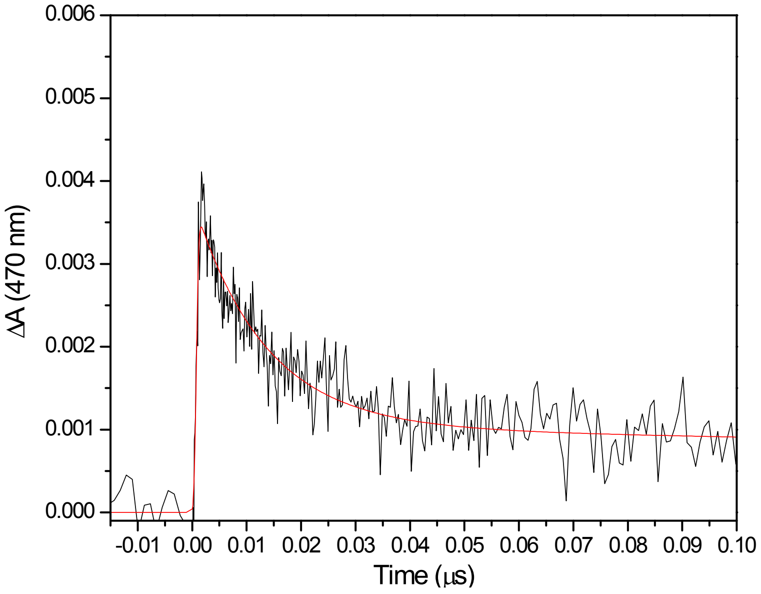

Figure S4: Decay of transient absorbance (ΔA) at 470 nm of 10^{-5} M PyCl in acetonitrile as a function of probe-delay time. The ΔA decay was fit with a monoexponential decay function.

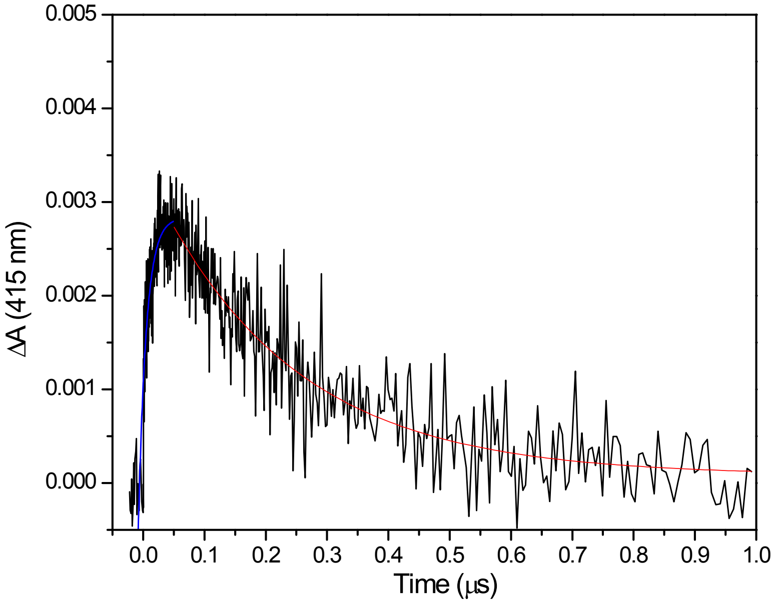

Figure S5: Rise and decay of transient absorbance (ΔA) at 415 nm of 10^{-5} M PyCl in acetonitrile as a function of probe-delay time. ΔA decay was fit with a monoexponential growth function and monoexponential decay function.

Table S1: Time constants (ns) and normalized pre-exponential factors (in parentheses) from emissions of 10^{-5} M ArCl and ArA in 1,4-dioxane at 293 K.

ArCl	$\tau_{Ex\ 1}$	$\tau_{Ex\ 2}$	ArA	$\tau_{Ex\ 1}$	$\tau_{Ex\ 2}$
PyCl[a]	2.2 (-0.69)	36.2 (0.31)	PyA[a]	1.4 (-0.04)	36.7 (0.96)
AnCl[b]	1.0 (-0.18)	7.6 (0.82)	AnA[b]	1.0 (-0.36)	7.7 (0.74)
NapCl[c]	6.7 (-0.18)	72.8 (0.51)	NapA[c]	4.9 (-0.19)	64.7 (0.81)

a) λ_{LE} = 377 nm, λ_{Ex} = 500 nm, $\lambda_{Excitation}$ = 344 nm

b) λ_{LE} = 391 nm, λ_{Ex} = 500 nm, $\lambda_{Excitation}$ = 369 nm

c) λ_{LE} = 350 nm, λ_{Ex} = 450 nm, $\lambda_{Excitation}$ = 305 nm

Table S2: Time constants (ns) and normalized pre-exponential factors (in parentheses) from emissions of 10^{-5} M ArCl in tetrahydrofuran at 293 K.

ArCl	$\tau_{LE\ 1}$	$\tau_{LE\ 2}$	$\tau_{LE\ 3}$	$\tau_{Ex\ 1}$	$\tau_{Ex\ 2}$
PyCl[a]	1.8 (0.87)	12.8 (0.11)	156.6 (0.02)	1.6 (-0.51)	14.4 (0.49)
AnCl[b]	2.1 (0.09)	6.7 (0.91)	-	-	-
NapCl[c]	4.1 (0.64)	31.7 (0.36)	-	3.7 (-0.46)	71.0 (0.39)

a) λ_{LE} = 377 nm, λ_{Ex} = 500 nm, $\lambda_{Excitation}$ = 344 nm

b) λ_{LE} = 391 nm, $\lambda_{Excitation}$ = 369 nm

c) λ_{LE} = 350 nm, λ_{Ex} = 450 nm, $\lambda_{Excitation}$ = 305 nm

Table S3: Time constants (ns) and normalized pre-exponential factors (in parentheses) from emissions of 10^{-5} M ArCl in acetonitrile at 293 K.

ArCl	$\tau_{LE\ 1}$	$\tau_{LE\ 2}$	$\tau_{LE\ 3}$
PyCl[a]	2.6 (0.74)	12.0 (0.24)	216.9 (0.02)
AnCl[b]	6.7 (1)	-	-
NapCl[c]	6.5 (0.97)	31.0 (0.03)	-

a) λ_{LE} = 377 nm, $\lambda_{Excitation}$ = 344 nm

b) λ_{LE} = 391 nm, $\lambda_{Excitation}$ = 369 nm

c) λ_{LE} = 350 nm, $\lambda_{Excitation}$ = 305 nm