Electronic Supplementary Material (ESI) for Materials Advances.

SI

Efficient construction of redox responsive thin polymer layer on glassy carbon and gold surfaces for voltage-gated delivery applications

Anna Barosi,[1] Avni Berisha,[2] Claire Mangeney,[1] Jean Pinson,[3] Hamid Dhimane,[1] Peter I. Dalko[1]

[1] Université de Paris, Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, CNRS UMR 8601, 45 rue des Saints-Pères, F-75270 Paris, France; e-mail: claire.mangeney@parisdescartes.fr, peter.dalko@parisdescartes.fr;

[2] University of Prishtina, Chemistry Department of Natural Sciences Faculty, rr. "Nëna Tereze" nr. 5, 10000 Prishtina, Kosovo

[3] Université de Paris, ITODYS, CNRS, UMR 7086, 15 rue J-A de Baïf, F-75013 Paris, France; e-mail: jean.pinson@univ-paris-diderot.fr

Table of contents:

General

Thin-layer chromatography was performed on aluminium-backed Merck Kieselgel 60 F_{254} pre-coatedplates. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 250 spectrometer (250 MHz and 63 MHz) and on a Bruker AV-500 spectrometer (500 MHz and 125 MHz). Chemical shifts for proton sare reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual proton in the NMR solvent ($CDCl_3$: δ 7.26, CD_3CN: δ 1.94). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.16, CD_3CN: δ 118.26). Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quadruplet, qn = quintuplet, b = broad, m = multiplet), coupling constants in Hertz (Hz). All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. The mass analyser was an Agilent from ThermoFisher. The capillary tension was 3.5 kV. The cone tension was 24 V. The temperature of the source was 130 °C and the temperature of desolvatation was 350 °C. Data were treated on ThermoQuest.

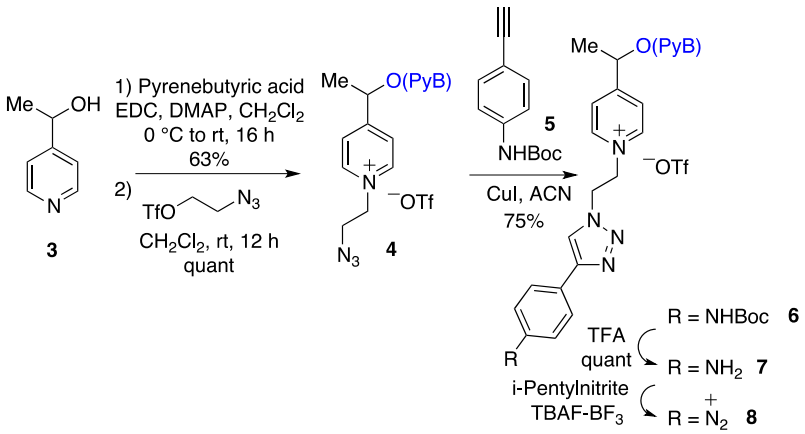
HPLC analyses were carried out on Water 515 device with a normal inverse phase column X-Terra® MS C18 (length: 75 mm, diameter: 4.6 mm, stationary phase: 2.5 µm) using a Waters 2487 Dual Absorbance Detector (260-360 nm) and an isocratic system of elution (MeOH-MeCN-H_2O 7-2-1 / H_2O $AcONH_4$ (10 mM) pH 4.6). The volume of injection was 10 µL.

Electrochemical experiments were performed with an EG&G 263A potentiostat/galvanostat and an Echem 4.30 version software. All potentials are referred to the Ag/AgCl electrode. The electrode for cyclic voltammetry was a glassy carbon (GC) rod (d =2 mm diameter) sealed in glass. It was polished with different grades of polishing papers and finally with a 0.04 µm alumina slurry on a polishing cloth (DP-Nap, Struers, Denmark), using a Presi Mecatech 234 polishing machine. Grafting was achieved on Au coated (100 nm) Si wafers obtained from Sigma-Aldrich. Before modification, they were rinsed in concentrated sulfuric acid, ultrasonicated in Milli-Q water for 6 min, cleaned with pure ethanol, and dried under a stream of argon. For the formation of the diazonium salt ***8*,** the ammonium salts of ***7*** were dissolved in ACN + 0.1M NBu_4BF_4 (c = 2 mM). Isopentylnitrite (c= 2.4 mM) was then added and let to react for 30 min before the experiments started. All the electrochemical experiments were performed in ACN + 0.1M NBu_4BF_4, deoxygenated with argon.

The IRRAS and ATR Spectra of modified plates were recorded using a purged (low CO_2, dry air) Jasco FT/IR-6100 Fourier Transform InfraRed Spectrometer equipped with MCT (mercury−cadmium−telluride) detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm^{-1}. The background recorded before each spectrum was that of a clean substrate. ATR spectra were recorded with a germanium ATR accessory (Jasco ATR PR0470-H). X-ray photoelectron spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a microfocused, monochromatic Al Kα X-ray source (1486.6 eV) and a magnetic lens, which increases the electron acceptance angle and hence the sensitivity. The pass energy was set at 150 and 40 eV for the survey and the narrow regions, respectively. The Avantage Software, version 4.67, was used for digital acquisition and data processing. The spectra were calibrated against C 1s set at 285 eV. Thicknesses of the films on Au were measured with a mono wavelength ellipsometer Sentech SE400. The following values were taken for gold ns = 0.17, ks = 3.43; they were measured on the clean surfaces before grafting. The film thicknesses were determined from the same plates after modification, taking ns = 1.46, ks = 0 for the organic layer. Raman spectra were recorded using an XploRA confocal Raman instrument (HORIBA Jobin Yvon) with a 638 nm laser as the source, in backscattering mode. All spectra were taken with a 3 s integration time and recorded within

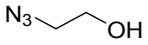
the 120−1750 cm^{-1} spectral range. The grafted Au_{20} mono charged gold cluster **9@Au** was modeled and used to calculate the Raman spectra. Calculations were performed with Dmol3 through generalized gradient approximations (GGE) using PBE functional[1] and DNP basis set (all electron core treatment). Self-consistent iteration method (SCF)[2] was used for geometry optimization (1000 iteration steps, using energy convergence of 2.0 e^{-5} eV/atom).

I. Synthesis of 1-(2-azidoethyl)-4-(1-((4-(pyren-1-yl)butanoyl)oxy)ethyl)-pyridin-1-ium trifluoromethanesulfonate (8)



Scheme S1. Synthesis of monomer **8**.

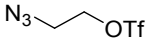
2-Azidoethanol[3]



A mixture of 2-chloroethanol (2 g, 24.8 mmol, 1 eq.), NaN_3 (2.1 g, 32.2 mmol, 1.3 eq.) and $n$$Bu_4NBr$ (200 mg, 0.62 mmol, 2.5 mol%) was stirred for 15 h at 110 °C (safety shield). After cooling, the product was taken up with Et_2O (20 mL) and the precipitate of NaCl, remaining NaN_3 and the phase transfer catalyst were filtered off. The salts were washed with Et_2O (20 mL). The solvent was then removed under reduced pressure and the compound was obtained as a colorless liquid (2.15 g, quant.).

NMR ^{1}H ($CDCl_3$, 250MHz): δ 3.80 (2H, t, J = 4.75 Hz), 3.46 (2H, t, J = 5.25 Hz), 2.30 (1H, bs). **NMR ^{13}C** ($CDCl_3$, 63MHz): δ 61.4, 53.4. **MS (ESI)**: m/z =88.0 $[M+H]^+$.

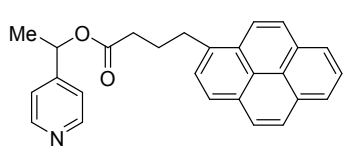
2-Azidoethyl trifluoromethanesulfonate



Triflic anhydride (1.56 g, 5.52 mmol, 1.2 eq.) was added at 0 °C to a solution of 2-azidoethan-1-ol (0.4 g, 4.6 mmol, 1 eq.) in DCM (4 ml). The mixture was stirred for 2 h at rt and then washed with water (3 x 15 ml). The organic layer was washed with brine (10 mL), dried with Na_2SO_4 and concentrated via rotary evaporation giving the title compound (0.97g, 97%).

NMR ^{1}H ($CDCl_3$, 500MHz): δ 4.63 (2H, t, J = 3.5 Hz), 3.71 (2H, t, J = 5 Hz). **NMR ^{13}C** ($CDCl_3$, 63MHz): δ 61.7, 49.1.

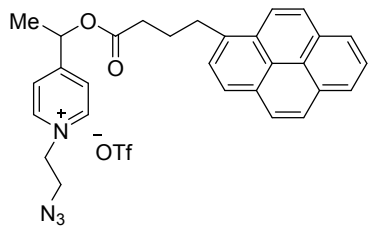
1-(Pyridin-4-yl)ethyl 4-(pyren-1-yl)butanoate (3)



In a two-necked flask under argon, 1-(pyridin-4-yl)ethan-1-ol[4] (0.20 g, 1.22 mmol, 1.1 eq.) and 4-(1-pyrenyl)butyric acid (0.320 g, 1.10 mmol, 1 eq.) were dissolved in DCM (4 ml). At 0 °C *N*-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC. HCl) (0.421 g, 2.2 mmol, 2 eq.), and DMAP (catalytic amount) were added and the reaction mixture was allowed to stir for 24 h. The solvent was removed via rotary evaporation and the crude purified by chromatography on silica gel column (DCM:MeOH, 9:1) to obtain the title compound (0.270 g, 63%).

NMR ^{1}H ($CDCl_3$, 500MHz): δ 8.57 (2H, dd, *J* = 4.5, 1.5 Hz), 8.28-8.25 (1H, m), 8.17 (2H, d, *J* = 8 Hz), 8.10 (2H, t, *J* = 8 Hz), 8.03 (2H, s), 8.00 (1H, t, *J* = 7.5 Hz), 7.85 (1H, m), 7.23-7.22 (2H, m), 5.86 (1H, q, *J* = 6.5 Hz), 3.40 (2H, t, *J* = 7.5 Hz), 2.54-2.50 (2H, m), 2.22 (2H, qn, *J* = 6.5 Hz), 1.52 (3H, d, *J* = 6.5 Hz). **NMR ^{13}C** ($CDCl_3$, 125MHz): δ 172.6, 150.6, 150.3, 150.2, 135.6, 131.6, 131.0, 130.2, 129.3, 128.9, 127.6, 127.5, 127.0, 126.0, 125.3, 125.1, 125.0, 123.3, 122.0, 120.8, 70.9, 34.1, 32.8, 26.7, 22.11. **MS (ESI)**: *m/z* =394.1 $[M+H]^+$. **HRMS (ESI):** m/z calcd for $[C_{27}H_{23}O_2N]^+$ 393.1729, found 393.1735

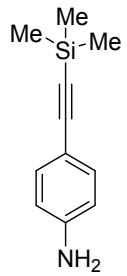
1-(2-Azidoethyl)-4-(1-((4-(pyren-1-yl)butanoyl)oxy)ethyl)pyridin-1-ium trifluoromethanesulfonate (**4**)



1-(Pyridin-4-yl)ethyl 4-(pyren-1-yl)butanoate (0.2 g, 0.5 mmol, 1 eq.) and 2-azidoethyl trifluoromethanesulfonate (0.144 g, 0.66 mmol, 1.3 eq.) were dissolved in DCM (1 ml) and stirred at rt for 16 h protected from light. After evaporation to dryness the crude product was purified by column chromatography on silica gel (DCM/MeOH 95/5) to obtain **4** (0.244 g, 0.53 mmol, quant.).

NMR ^{1}H ($CDCl_3$, 500MHz): δ 8.69 (2H, d, *J* = 6.5 Hz), 8.25 (1H, d, *J* = 9 Hz), 8.17 (2H, d, *J* = 8 Hz), 8.11-8.09 (2H, m), 8.03-7.98 (3H, m), 7.84 (1H, d, *J* = 8 Hz), 7.64 (2H, d, *J* = 6.5 Hz), 5.7 (1H, q, *J* = 6.8 Hz), 4.69-4.66 (2H, m), 3.93 (2H, t, *J* = 5.5 Hz), 3.48-3.40 (2H, m), 2.55 (2H, t, *J* = 7.5 Hz), 2.24 (2H, qn, *J* = 7.5 Hz), 1.65-1.55 (2H, m), 1.46 (3H, d, *J* = 6.5 Hz). **NMR ^{13}C** ($CDCl_3$, 125MHz): δ 172.2, 161.9, 145.2, 135.2, 131.5, 131.0, 130.2, 129.4, 128.9, 128.0, 127.7, 127.6, 127.0, 126.2, 125.7, 125.2, 125.1, 125.0, 124.6, 123.3, 69.9, 60.5, 50.7, 33.8, 32.7, 26.4, 21.7. **MS (ESI)**: *m/z* =463.4 $[M]^+$. **HRMS (ESI):** m/z calcd for $[C_{29}H_{27}O_2N_4]^+$ 463.2129, found 463.2137.

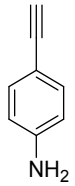
4-((Trimethylsilyl)ethynyl)aniline[5]



4-Iodoaniline (1.25 g, 5.7 mmol, 1 eq.) was dissolved in THF (10 ml) and TEA (10 ml) then CuI (54 mg, 0.28 mmol, 5 mol%) and $(Ph_3P)_2PdCl_2$ (200 mg, 0.28 mmol, 5 mol%) were added and the solution was stirred under Argon at rt for 30 min. Ethynyltrimethylsilane (835 mg, 8.55 mmol, 1.5 eq.) was then added and the mixture was stirred at 45 °C for 16 h. The solvent was removed and then the crude residue was purified by chromatography on a silica gel column (cyclohexane/EtOAc: 2/1) to give the title compound (1.07 g, 99%) as a off-white solid.

NMR ^{1}H ($CDCl_3$, 500MHz): δ 7.27 (2H, dd, *J* = 8.5, 1.5 Hz), 6.57 (2H, dd, *J* = 8.5, 1.5 Hz), 3.78 (2H, bs), 0.23 (9H, s). **NMR ^{13}C** ($CDCl_3$, 125MHz): δ 146.9, 133.5, 114.7, 112.7, 106.1, 98.7, 55.4, 5.6 (3C).

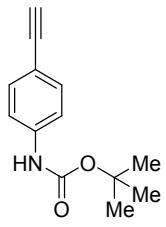
4-Ethynylaniline[3]



To a solution of 4-(trimethylsilylethynyl) aniline (1 g, 5.28 mmol, 1 eq.) in MeOH (5 mL), K_2CO_3 (1.45 g, 10.56 mmol, 2 eq.) was added and the resulting suspension was stirred at rt for 1 h. The solution was then taken to dryness under reduced pressure. The residue was then filtered through Celite. The solvent was removed under reduced pressure to obtain the desired compound (0.550 g, 89%).

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.29 (2H, d, *J* = 8.5 Hz), 6.59 (2H, d, *J* = 8.5 Hz), 3.33 (1H, s). **^{13}C NMR** ($CDCl_3$, 125MHz): δ 133.6, 118.8, 114.7, 111.6, 51.4, 50.9.

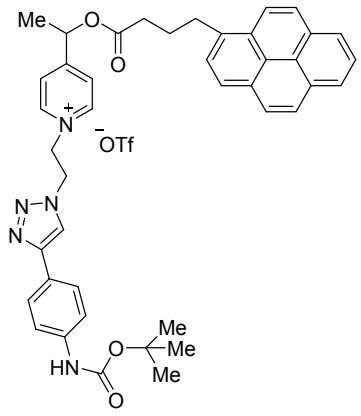
***tert*-Butyl (4-ethynylphenyl)carbamate** (**5**)[6]



To a solution of di-tert-butyl dicarbonate (Boc_2O) (1.33 g, 6.09 mmol, 1.3 eq.) in 10 mL THF was added 4-ethynylaniline (0.55 g, 4.69 mmol, 1 eq.). Solution was stirred and refluxed for 16 h. The solvent was removed in vacuum, and the product was purified by chromatography on a silica gel column (Cyclohexane/EtOAc : 2/1) to give the desired compound (**5**) (0.7 g, 70 %)

NMR ^{1}H ($CDCl_3$, 500MHz): δ 7.41 (2H, d, *J* = 8.5 Hz), 7.32 (2H, d, *J* = 8.5 Hz), 6.51 (1H, bs), 3.01 (1H, s), 1.52 (9H, s). **NMR ^{13}C** ($CDCl_3$, 125MHz): δ 152.5, 139.0, 133.1, 118.1, 116.5, 83.7, 81.1, 76.4, 28.5.

1-(2-(4-(4-((*tert*-Butoxycarbonyl)amino)phenyl)-1H-1,2,3-triazol-1-yl)ethyl)-4-(1-((4-(pyren-1-yl)butanoyl)oxy)ethyl)pyridin-1-ium trifluoromethanesulfonate (**6**)

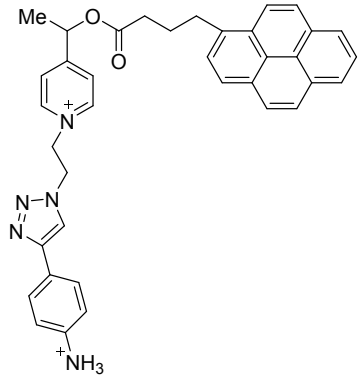


1-(2-azidoethyl)-4-(1-((4-(pyren-1-yl)butanoyl)oxy)ethyl)pyridin-1-ium trifluoromethanesulfonate **4** (0.200g, 0.32 mmol), *tert*-butyl (4-ethynylphenyl)carbamate, **5** (0.106 g, 0.48 mmol) and CuI (0.006 g, 10% mol.) were dissolved in ACN (1 mL). The reaction mixture was stirred for 20 h at rt. After evaporation to dryness the crude product was purified by column chromatography on silica gel (DCM/MeOH 95/5) to obtain **6** (0.2 g, 0.24 mmol, 75%).

NMR ^{1}H ($CDCl_3$, 500MHz): δ 8.53 (2H, d, *J* = 6.8 Hz), 8.17 (1H, d, *J* = 9.5 Hz), 8.10 (2H, d, *J* = 7.5 Hz), 8.05-8.01 (3H, m), 7.95-7.92 (3H, m), 7.75 (1H, d, *J* = 8 Hz), 7.57 (2H, d, *J* = 8.5 Hz), 7.51 (2H, d, *J* = 6.5 Hz), 7.30 (2H, d, *J* = 8.5 Hz), 6.73 (1H, s), 5.60 (1H, q, *J* = 6.5 Hz), 5.15-5.12 (2H, m), 5.00-4.98 (2H, m), 3.37-3.24 (2H, m), 2.44 (2H, t, *J* = 7 Hz), 2.12 (2H, qn, *J* = 7 Hz), 1.48 (9H, s), 1.32 (3H, d, *J* = 6.5 Hz). **NMR ^{13}C** ($CDCl_3$, 125MHz): δ 172.1, 161.9, 152.9, 148.0, 146.9, 145.1, 138.8, 135.3, 131.4, 130.9, 130.1, 128.8, 127.6, 127.5,

126.9, 126.4, 126.1, 125.1-124.7 (7C), 123.3, 122.0, 119.4, 69.8, 60.3, 36.4, 33.7, 32.6, 28.5, 26.3, 21.5, 14.9. **MS (ESI)**: *m/z* =680.1 $[M]^+$. **HRMS (ESI):** m/z calcd for $[C_{42}H_{42}O_4N_5]^+$ 680.3231, found 680.3224.

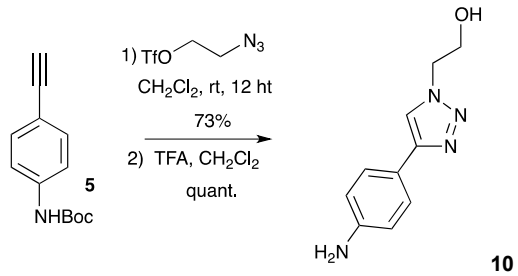
1-(2-(4-(4-Ammoniophenyl)-1H-1,2,3-triazol-1-yl)ethyl)-4-(1-((4-(pyren-1-yl)butanoyl)oxy)ethyl)pyridin-1-ium (**7**)



Compound **6** (0.195 g, 0.23 mmol, 1 eq.) was dissolved in 1 ml DCM and TFA (0.535g, 4.7 mmol, 20 eq., d=1.49 g/ml) was added. The mixture was allowed to stir at rt for 12h. After evaporation to dryness the product was filtered on silica gel to obtain the desired compound (0.133 g, quant.).

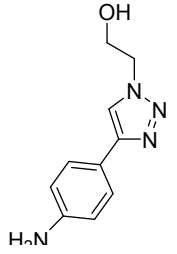
NMR ^{1}H ($CDCl_3$, 250MHz): δ 8.55 (2H, d, *J* = 6.8 Hz), 8.32 (1H, s), 8.13 (1H, d, *J* = 6.8 Hz), 8.05 (2H, d, *J* = 8.3 Hz), 8.00-7.85 (7H, m), 7.71 (3H, m), 7.41 (2H, d, *J* = 8.5 Hz), 5.65 (1H, q, *J* = 6.8 Hz), 5.01 (4H, m), 3.26-3.17 (2H, m), 2.45 (2H, t, *J* = 7 Hz), 2.04 (2H, qn, *J* = 7 Hz), 1.35 (3H, d, *J* = 6.8 Hz). **NMR ^{13}C** ($CDCl_3$, 125MHz): δ 173.7, 164.0, 149.4, 146.2, 136.9, 132.8, 132.2, 131.4, 129.9, 128.7, 128.6, 128.4, 127.9, 127.7, 127.3, 127.1, 126.1-125.9 (5C), 124.4, 124.2, 123.1, 122.4, 119.0, 71.4, 61.3, 50.9, 34.5, 33.5, 27.6, 21.7. **MS (ESI)**: *m/z* =581.1 $[M]^+$. **HRMS (ESI):** m/z calcd for $[C_{37}H_{35}O_2N_5]^+$ 581.2780, found 581.2771

II. Synthesis of fragments



Scheme S2. Synthesis of the alkylating chain fragment.

2-(4-(4-Aminophenyl)-1H-1,2,3-triazol-1-yl)ethan-1-ol (**10**)



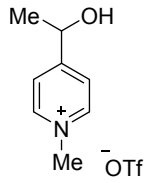
2-Azidoethyl trifluoromethanesulfonate (0.017 g, 0.18 mmol, 1 eq.), *tert*-butyl (4-ethynylphenyl)carbamate (0.06 g, 0.27 mmol, 1.5 eq.) and CuI (10% mol) were dissolved in ACN (1 mL). The reaction mixture was stirred for 24 h at rt. After evaporation to dryness the crude product was purified by column chromatography on silica gel (DCM/MeOH 95/5) to obtain the title compound (0.04 g, 73%).

The Boc-protected compound (0.04 g, 0.13 mmol, 1 eq.) was dissolved in 1 ml DCM and TFA (0.299 g, 2.6 mmol, 20 eq., d = 1.49 g/ml) was added.

The mixture was allowed to stir at rt for 12h. After evaporation to dryness the product was filtered on silica gel to obtain the desired compound (0.03 g, quant.).

NMR ^{1}H (MeOD, 500 MHz): δ 8.44 (1H, s), 8.00 (2H, d, *J* = 9 Hz), 7.47 (2H, d, *J* = 8.5 Hz), 4.59 (2H, t, *J* = 5 Hz), 4.02 (2H, t, *J* = 5.5 Hz). **NMR ^{13}C** (MeOD, 125MHz): δ 147.2, 132.6, 123.3, 128.2, 124.3, 123.5, 61.6, 54.1. **MS (ESI)**: *m/z* =205.2 $[M+H]^{+}$.

4-(1-Hydroxyethyl)-1-methylpyridin-1-ium trifluoromethanesulfonate (**11**)[4]



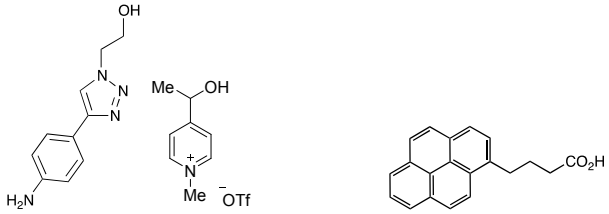
To a solution of 1-(pyridin-4-yl)ethan-1-ol (0.08 g, 0.65 mmol, 1 eq.) in dry dichloromethane (1 ml) is added methyl trifluoromethanesulfonate (80 µl, 0.71 mmol, 1.1 eq.). The mixture is allowed to stir at rt for 1 h, under argon and protected from light. The solvent is then evaporated and the product obtained is purified by chromatography on silica gel (DCM/MeOH 95:5) to obtain the title compound (0.14 g, 75%).

NMR ^{1}H (MeOD, 500 MHz): δ 8.82 (2H, d, *J* = 6.5 Hz), 8.09 (2H, d, *J* = 6.5 Hz), 5.12 (1H, q, *J* = 7 Hz), 4.40 (3H, s), 1.54 (3H, d, *J* = 6.5 Hz).

III. Voltammetry

In the voltammogram (Fig. 5) peak I_{red} corresponds to the reduction of the anilinium by comparison with the authentic sample, whereas IV_{ox} corresponds to the oxidation of the aniline. Peak II_{red} corresponds to the partly reversible reduction of the pyridinium group. Peaks III_{red} and III_{ox} correspond to the reversible couple pyrene/pyrene radical anion as compared to the voltammogram of pyrene butyric acid that exhibits the same reversible wave, and V_{ox} corresponds to the oxidation of the pyrene nucleus. The reversibility of the wave of pyrenebutyric acid indicates that the carboxylic function is not strong enough to protonate the radical anion of pyrene. This reversible couple, III_{red}/III_{ox}, involves the transfer of one electron (pyrene / pyrene$^{-\bullet}$), as reported previously.[18] By comparison with the other peaks in the voltammogram, displaying similar intensities, it can be concluded that they all involve the transfer of one electron.

Fragment	Peak potentials of fragment	Peak potentials of **7**
10	I_{red} = –0.92 V	I_{red} = –0.95 V
	IV_{ox} = +0.87 V	IV_{ox} = +0.90 V
11	II_{red} = –1.27 V	II_{red} = –1.30 V
12	III_{red} = –2.12 V	III_{red} = –2.15 V
	III_{ox} = –2.10 V	III_{ox} = –2.10 V
	V_{ox} = +1.28 V	V_{ox} = +1.45 V



10 **11** **12**

Table S1 Electrochemical profiles of the synthesized fragments of compound **7** and corresponding peak potential values in V/(Ag/AgCl) for compound **7**. The oxidation peak of the anilinium is not listed for sake of clarity. For voltammograms see Fig. S1-S4.

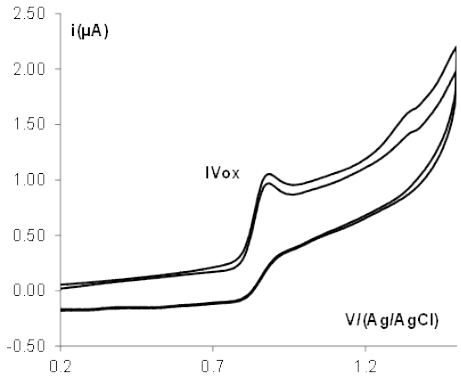


Figure S1. Oxidation peak of the aniline derivative (**10**), recorded on a GC electrode in ACN + 0.1M *n*-Bu_4NBF_4, with c = 2 mM, v = 0.1 Vs^{-1} (Ag/AgCl).

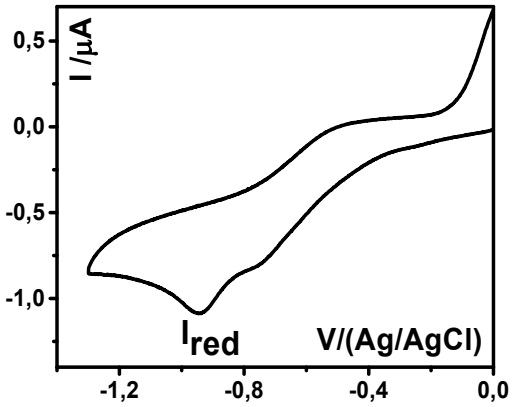


Figure S2. Voltammogram of the aniline derivative (**10**), recorded on a GC electrode in ACN + 0.1M *n*-Bu_4NBF_4, with c = 2 mM, v = 0.1 Vs^{-1} (Ag/AgCl).

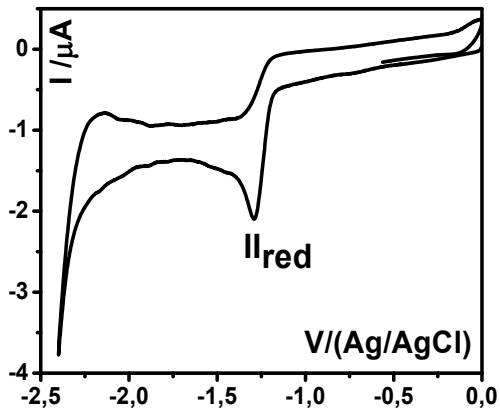


Figure S3. Voltammogram of the pyridynium derivative (**11**), recorded on a GC electrode in ACN + 0.1M *n*-Bu_4NBF_4, with c = 2 mM, v = 0.1 Vs^{-1} (Ag/AgCl).

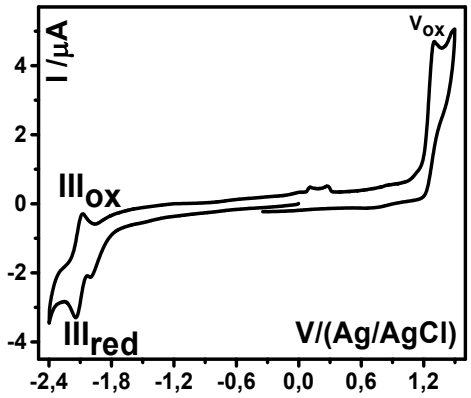


Figure S4. Voltammogram of the pyrenebutyric acid (**12**), recorded on a GC electrode in ACN + 0.1M *n*-Bu_4NBF_4, with c = 2 mM, v = 0.1 Vs^{-1} (Ag/AgCl).

IV. IR spectroscopy

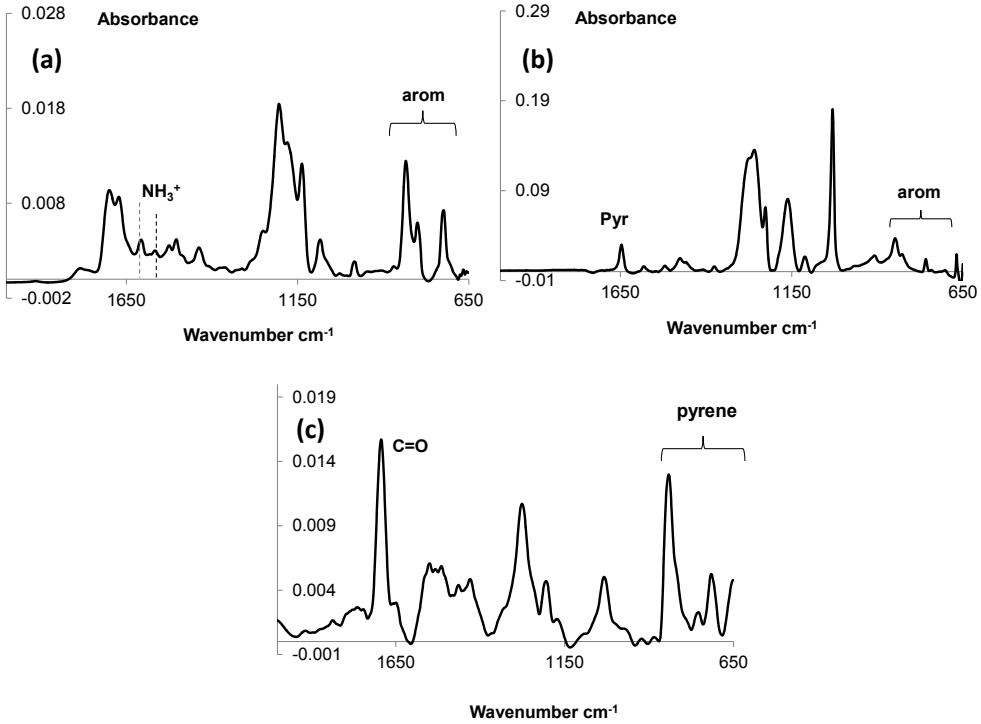


Figure S5. IR-ATR spectra of (a) the anilinium fragment (**10**) displaying typical NH_3^+ (NH deformation) and aromatic vibrations (out of plane aromatic bands); (b) the pyridinium fragment (**11**) displaying the pyridinium ring vibrations and aromatic vibrations (out of plane aromatic bands); (c) pyrenebutyric acid with the C=O carbonyl band and pyrene vibrations (C-H out of plane).

V. Fluorescence

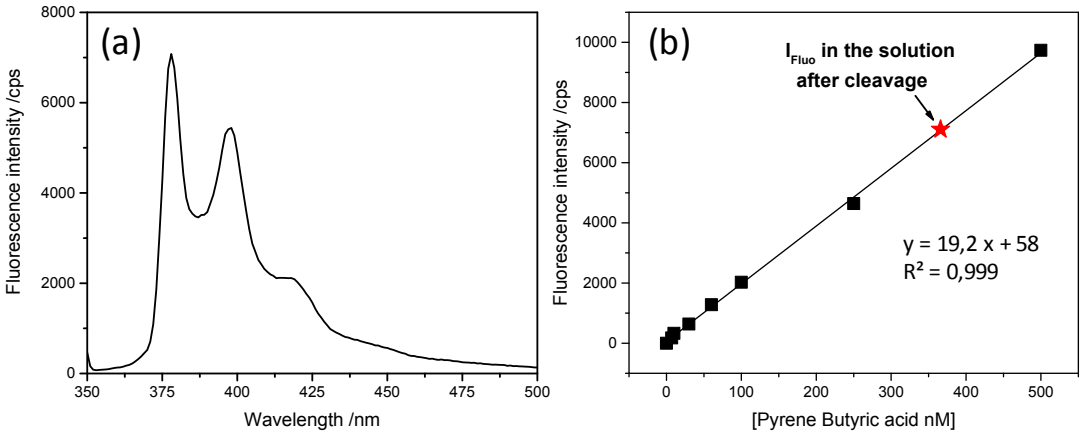
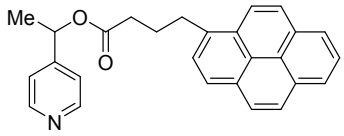
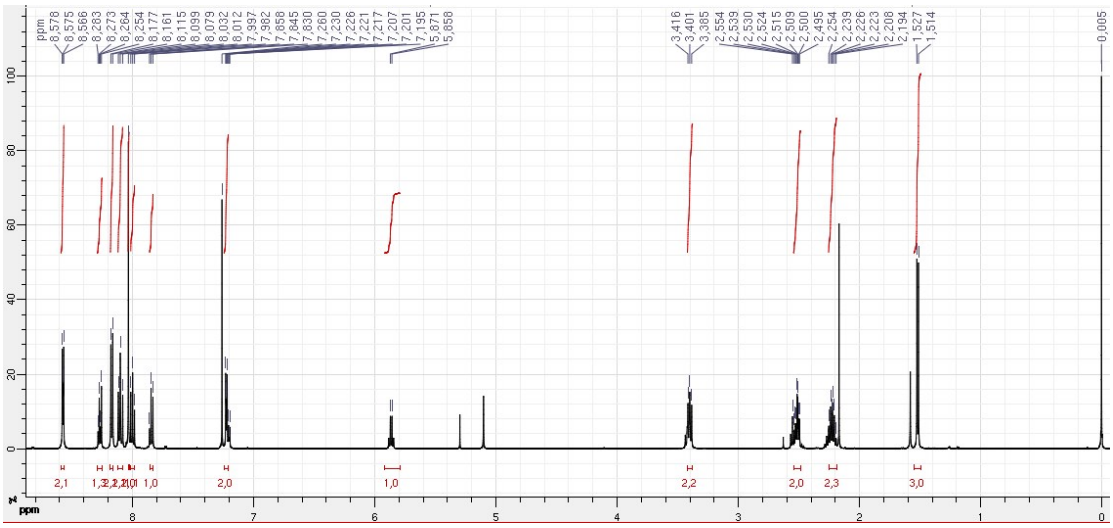


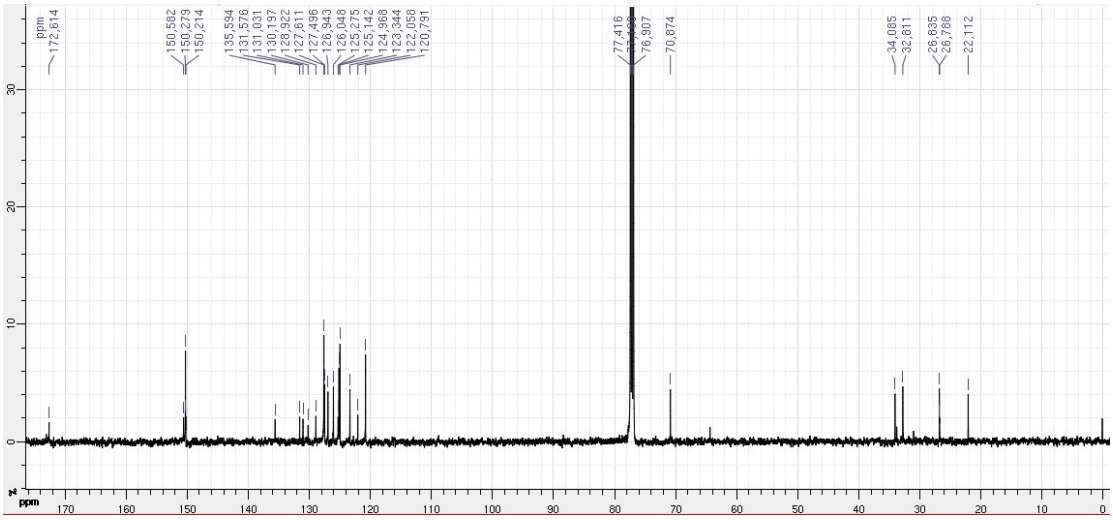
Figure S6. Fluorescence analysis of the released pyrene butyric acid moieties after ET-mediated fragmentation of the picolinium-derived probes immobilized on a gold electrode. (a) Fluorescence spectrum of the electrolysis solution containing the fluorescent probe; (b) Fluorescence calibration curve of pyrene butyric acid in ACN (excitation: λ_{341}, emission: λ_{379}).

NMR Spectra

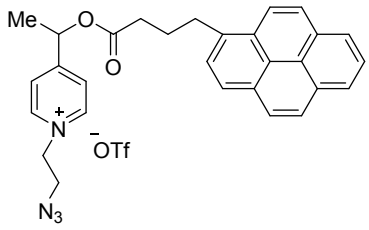
1-(Pyridin-4-yl)ethyl 4-(pyren-1-yl)butanoate

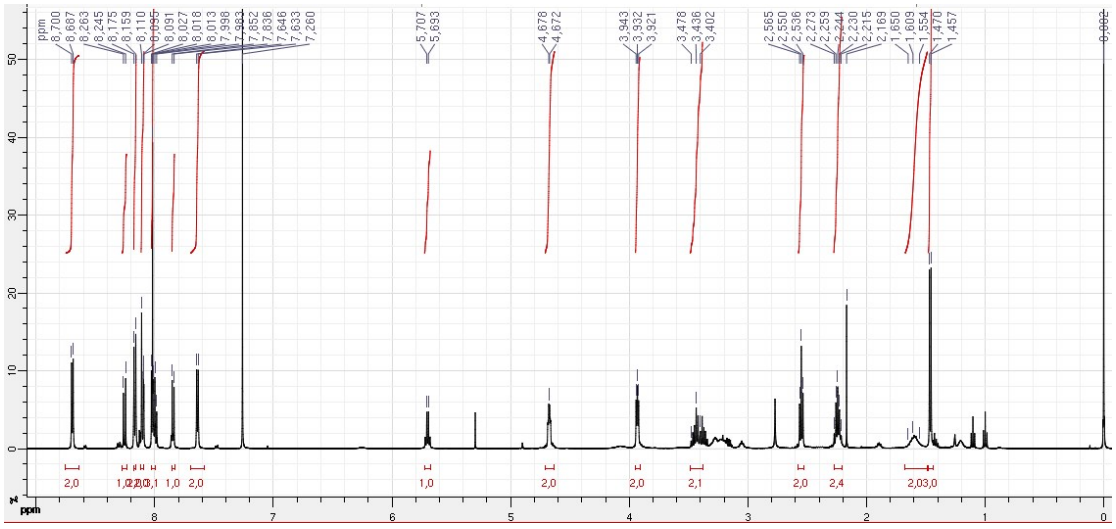


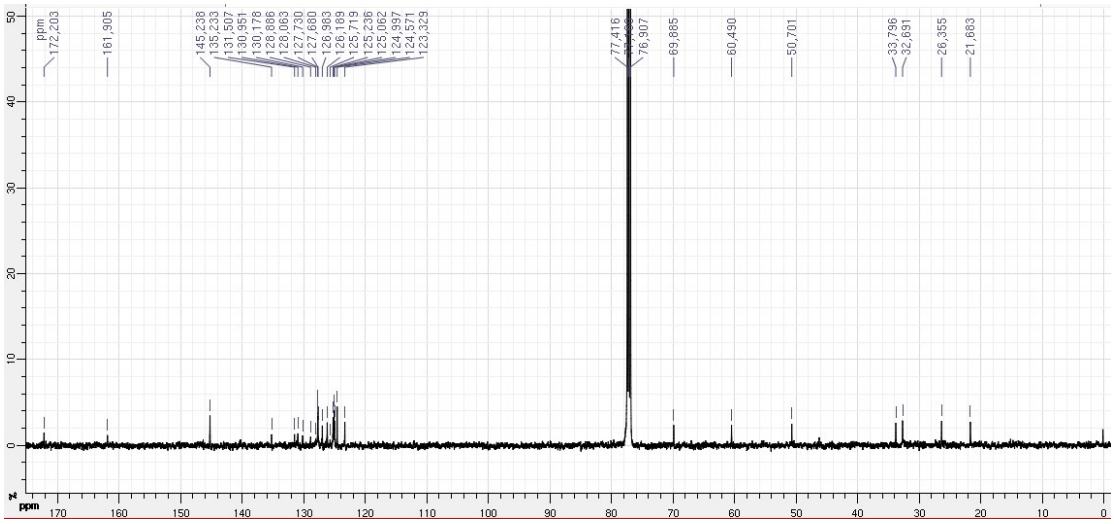




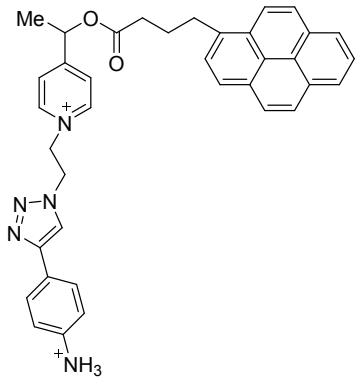
1-(2-Azidoethyl)-4-(1-((4-(pyren-1-yl)butanoyl)oxy)ethyl)pyridin-1-ium trifluoromethanesulfonate (4)

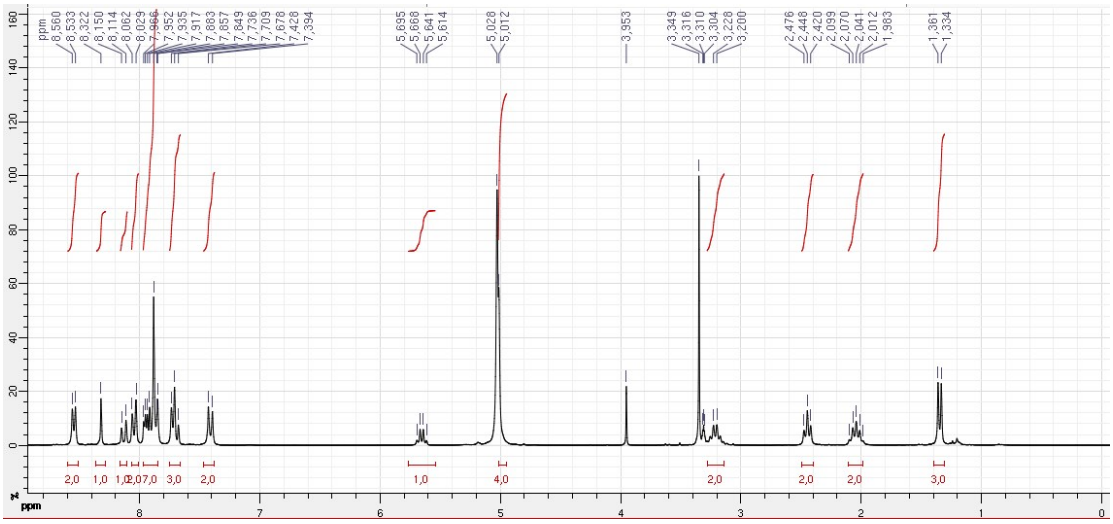


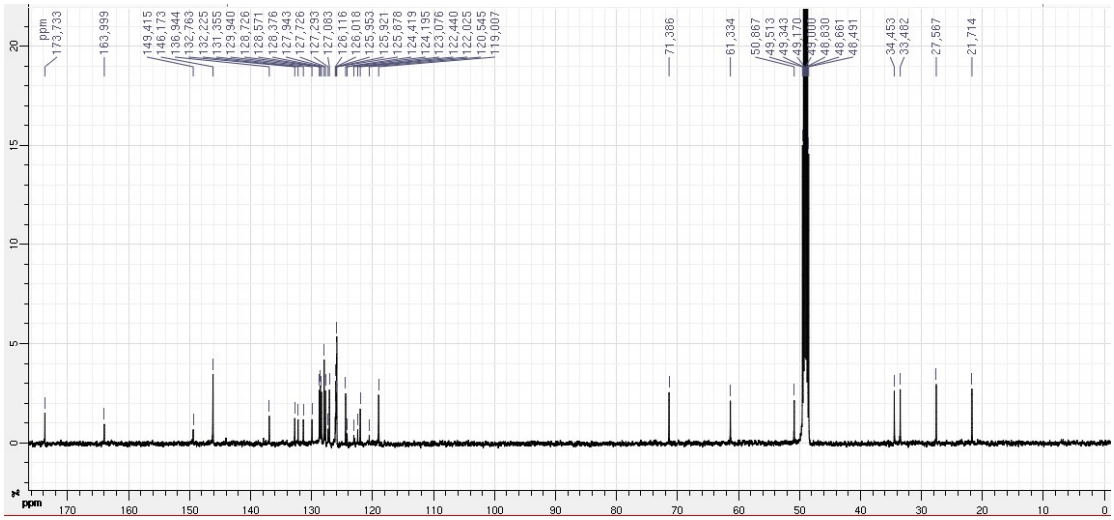




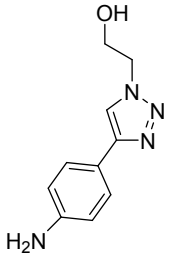
1-(2-(4-(4-Ammoniophenyl)-1H-1,2,3-triazol-1-yl)ethyl)-4-(1-((4-(pyren-1-yl)butanoyl)oxy)ethyl)pyridin-1-ium (7)

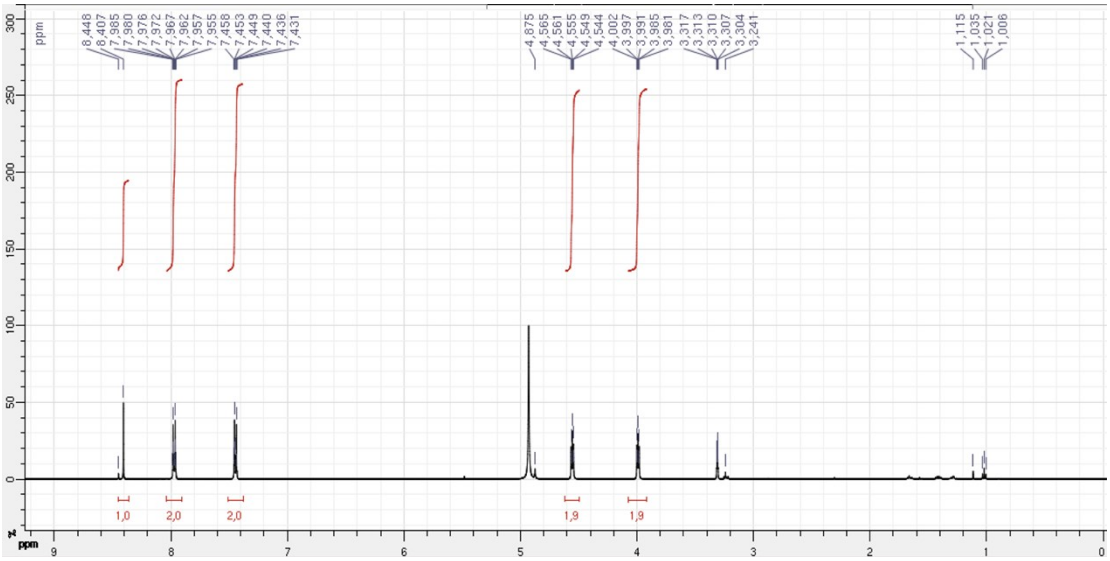


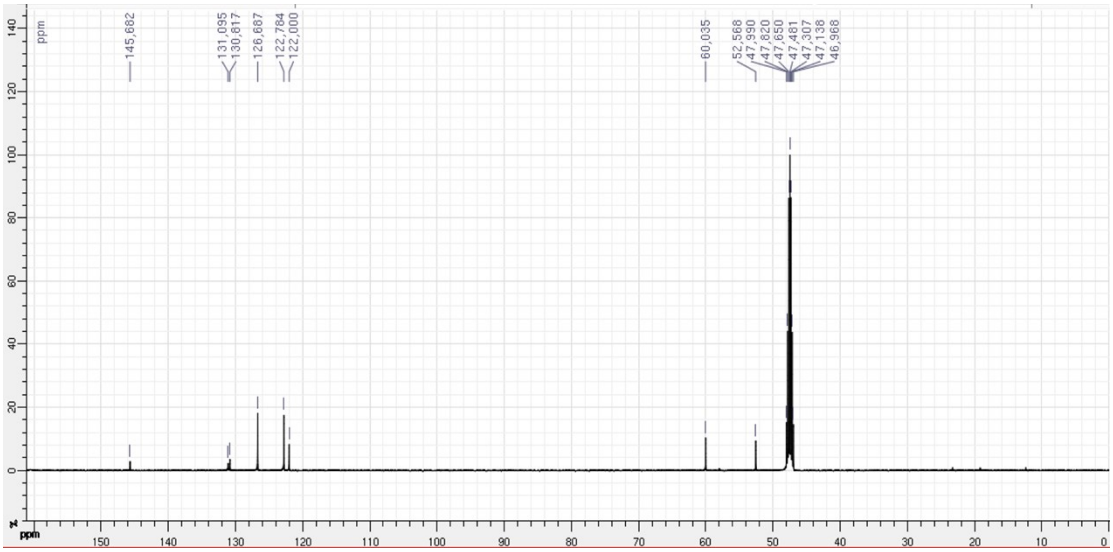




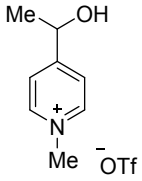
2-(4-(4-Aminophenyl)-1H-1,2,3-triazol-1-yl)ethan-1-ol

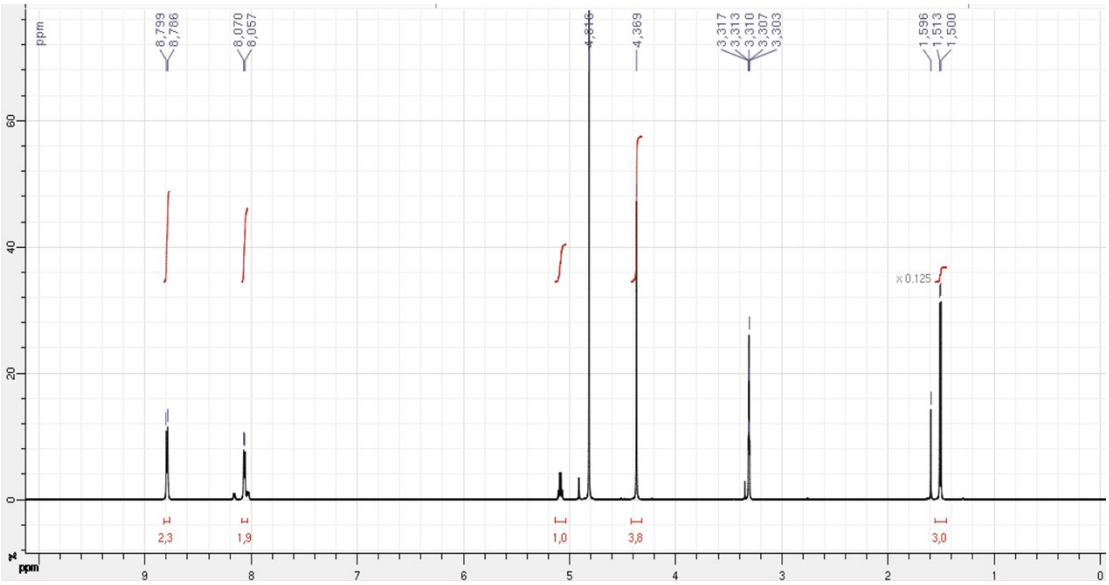






4-(1-Hydroxyethyl)-1-methylpyridin-1-ium trifluoromethanesulfonate[4]





VII. Redox potential calculation using DFT

The theoretical calculation of the standard redox potential in solution is based upon the use of the Born-Haber cycle (presented below).

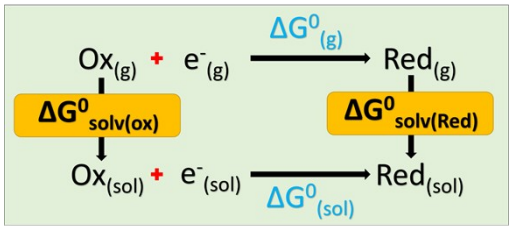


Figure S7. The thermodynamic cycle of the one-electron reduction of picolinium probes in acetonitrile (ACN) solution.

All theoretical calculations were performed with the Gaussian software[7]. The geometry optimizations is performed using B3LYP functional in combination with 6-311+g(d,p) basis set. The dispersion correction is based upon the Grimme's Dispersion DFT-D3 model. Solvent effects (acetonitrile) were included via the integral equation formalism variant (IEFPCM) approach[8].

References

[1] B. Hammer, L. B. Hansen, J. K. Nørskov, *Physical Review B* **1999**, *59*, 7413.

[2] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J. D. Joannopoulos, *Rev. Mod. Phys.* **1992**, *64*, 1045.

[3] W. S. Shin, S. K. Park, P. Verwilst, S. Koo, J. H. Lee, S.-G. Chi, J. S. Kim, *Chem. Commun*. **2017**, *53*, 1281 and references cited.

[4] P. Dunkel, A. Barosi, H. Dhimane, F. Maurel, P. I. Dalko, *Chem. Eur. J*., **2018**, *24*, 12920.

[5] Y. Arakawa, S. Kang, H. Tsuji, J. Watanabe, G.-i. Konishi, *RSC Adv.*, **2016**,*6*, 92845.

[6] C. P. Allen, T. Benkovics, A. K. Turek, T. P. Yoon, *J. Am. Chem. Soc*., **2009**, *131*, 12560.

[7] Gaussian 09 (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian Inc., Wallingford, CT, 2009.

[8] E. Cances, B. Mennucci, J. J. Tomasi, *Chem. Phys*. **1997**, *107*, 3032.