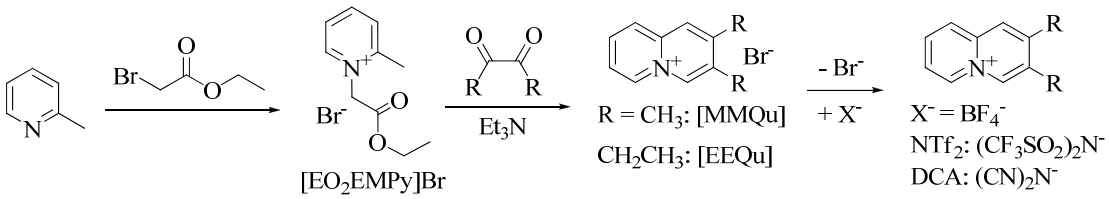
Supplementary Material for

Fluorescent quinolizinium ionic liquids (salts) with unexpectedly high quantum yields up to > 99%

*Zhengjian Chen, Shiguo Zhang, Xiujuan Qi, Shimin Liu, Qinghua Zhang and Youquan Deng**

Details on synthesis and characterization of quinolizinium salts



Scheme S1. Synthesis of quinolizinium ionic liquids (salts).

Chemicals. All commercially available chemicals and regents were purchased from Aldrich, Tianjin Chemical Reagent Corporation Ltd. or Nanjing Chemlin Chemical Industrial Co., as analytical or laboratory grade materials and used without further purification.

[EO_2EMPy]Br. The mixture of 1.0 mol α-methylpyridine, 1.0 mol ethyl 2-bromoacetate and 180 mL anhydrous ethanol was vigorously stirred at 60 ^oC for 5 h and 80 ^oC for 15 h. After reaction, ethanol was removed by evaporation in vacuum at 80 ^oC, and the residue became a pale yellow solid. 500 mL acetone and 100 mL diethyl ether was added to the solid, and the mixture was mechanically stirred at room temperature for 5 h. After filtration, washed with diethyl ether, and evaporation in vacuum at 80 ^oC, [EO_2EMPy]Br was obtained as white solid: 257 g (yield: 99%).

[MMQu]Br. The mixture of 0.60 mol 2,3-Butanedione and 0.60 mol Triethylamine was added dropwise to a solution of 0.50 mol [EO_2EMPy]Br in 1000 mL tetrahydrofuran under reflux, and then the mixture reacted under reflux for 3 hours. When the reaction was complete, the resulting solid was immediately collected by filtration, washed with boiling acetone. The solid was purified by recrystallization from methanol by addition of diethyl ether, and dried under a high vacuum. Pale yellow solid; yield: 92% (131 g); ^{1}H-NMR (DMSO, 400 MHz, ppm, Fig. S6): 9.350 (s, 1H, H-1), 9.232 (d, 1H, H-6), 8.411 (d, 2H, H-2,3), 8.269 (t, 1H, H-4), 7.999 (t, 1H, H-5), 2.597 (s, 3H, CH_3-7), 2.480 (s, 3H, CH_3-8); ^{13}C-NMR (DMSO, 400 MHz, ppm, Fig. S7): 149.9, 140.8, 135.7, 135.2, 134.7, 134.0, 125.8, 125.1, 122.7, 19.5, 16.5; FT-IR (cm^{-1}): 3063, 3029, 3007, 2979, 2949, 2917, 1647, 1634, 1622, 1495, 1479, 1469, 1453, 1431, 1406, 1384, 1332, 1311, 1179, 1158, 1031, 1020.

[EEQu]Br. The same procedure was followed as for [MMQu]Br, except that 3,4-Hexanedione was used instead of 2,3-Butanedione. White solid; yield: 91%; ^{1}H-NMR (DMSO, 400 MHz, ppm, Fig. S8): 9.347 (d, 1H, H-6), 9.296 (s, 1H, H-1), 8.498 (d, 1H, H-3), 8.444 (s, 1H, H-2), 8.291 (t, 1H, H-4), 8.020 (t, 1H, H-5), 2.948 (m, 4H, CH_2-7,8), 1.364 (m, 6H, CH_3-9,10); ^{13}C-NMR

(DMSO, 400 MHz, ppm, Fig. S9): 153.9, 141.0, 138.9, 135.7, 135.4, 133.5, 126.0, 123.5, 122.7, 24.5, 22.5, 12.8, 12.5; FT-IR (cm^{-1}): 3125, 3056, 3024, 2970, 2942, 2884, 1645, 1630, 1482, 1466, 1443, 1387, 1340, 1311, 1245, 1146, 1068, 1028.

[MMQu]NTf_2. The same procedure was followed as described for [MMQu]BF_4, except 0.18 mol $LiNTf_2$ of aqueous solution was used instead of saturated $NaBF_4$ aqueous solution. White solid; yield: 93%; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm, referring to Fig. S6): 8.998 (d, 1H, H-6), 8.887 (s, 1H, H-1), 8.186 (d, 1H, H-3), 8.086 (q, 2H, H-2,4), 7.770 (t, 1H, H-5), 2.619 (s, 3H, CH_3-7), 2.544 (s, 3H, CH_3-8); FT-IR (cm^{-1}): 3097, 3049, 2991, 2968, 2925, 2861, 1650, 1496, 1483, 1469, 1449, 1432, 1407, 1386, 1349, 1333, 1314, 1274, 1190, 1160, 1135, 1062, 1028; ESI-MS (*m*/*z*): 158.0969 with a calculated value of 158.10 for $[C_{11}H_{12}N]^+$.

[EEQu]NTf_2. See the procedure described for [MMQu]NTf_2. White solid; yield: 93%; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm, referring to Fig. S8): 9.087 (d, 1H, H-6), 8.847 (s, 1H, H-1), 8.226 (d, 1H, H-3), 8.107 (t, 1H, H-4), 8.061 (s, 1H, H-2), 7.795 (t, 1H, H-5), 2.956 (m, 4H, CH_2-7,8), 1.425 (m, 6H, CH_3-9,10); FT-IR (cm^{-1}): 3140, 3109, 3058, 2978, 2946, 2889, 1653, 1639, 1495, 1479, 1450, 1410, 1384, 1350, 1331, 1196, 1138, 1056. ESI-MS (*m*/*z*): 186.1281 with a calculated value of 186.13 for $[C_{13}H_{16}N]^+$.

[MMQu]BF_4. With the addition of 0.15 mol [MMQu]Br to 100 mL saturated $NaBF_4$ aqueous solution, a white precipitate occurred immediately. The mixture was vigorously stirred at room temperature for 5 hours. After filtration, washed with 1 M $NaBF_4$ aqueous solution and distilled water, the desired salt was obtained, followed by evaporation at 100 ^{o}C and reduced pressure. White solid; yield: 81% (30 g); ^{1}H-NMR (CD_3OCCD_3, 400 MHz, ppm, referring to Fig. S6): 9.251 (s, 1H, H-1), 9.222 (d, 1H, H-6), 8.479 (d, 1H, H-3), 8.451 (s, 1H, H-2), 8.353 (t, 1H, H-4), 8.059 (t, 1H, H-5), 2.734 (s, 3H, CH_3-7), 2.650 (s, 3H, CH_3-8); FT-IR (cm^{-1}): 3107, 3094, 3074, 3045, 3008, 2992, 1646, 1495, 1482, 1448, 1434, 1406, 1386, 1313, 1288, 1164, 1183, 1058.

[EEQu]BF_4. See the procedure described for [MMQu]BF_4. White solid; yield: 93%; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm, referring to Fig. S8): 9.178 (d, 1H, H-6), 9.036 (s, 1H, H-1), 8.286 (d, 1H, H-3), 8.147 (s, 1H, H-2), 8.115 (t, 1H, H-4), 7.793 (t, 1H, H-5), 2.947 (m, 4H, CH_2-7,8), 1.420 (m, 6H, CH_3-9,10); FT-IR (cm^{-1}): 3148, 3094, 3056, 2970, 2944, 2886, 1646, 1637, 1479, 1494, 1466, 1442, 1409, 1385, 1338, 1316, 1288, 1060.

[MMQu]DCA. 0.18 mol AgDCA, followed by 0.15 mol [MMQu]Br, was added into 300 mL distilled water under vigorous stirring at ambient temperature. After reaction for 2 h, the mixture was filtrated and washed with distilled water (4 × 100 mL). The filtrate was then concentrated by rotary evaporation and further dried in vacuum at 80 ^{o}C. Pale yellow solid; yield: 85%; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm, referring to Fig. S6): 9.179 (d, 1H, H-6), 9.159 (s, 1H, H-1), 8.255 (d, 1H, H-3), 8.160 (t, 2H, H-2,4), 7.854 (t, 1H, H-5), 2.678 (s, 3H, CH_3-7), 2.619 (s, 3H, CH_3-8). FT-IR (cm^{-1}): 3029, 3981, 2288, 2231, 2197, 2135, 1649, 1494, 1406, 1382, 1308, 1157, 1030.

[EEQu]DCA. See the procedure described for [MMQu]DCA. Pale yellow solid; yield: 86%; ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm, referring to Fig. S8): 9.9285 (d, 1H, H-6), 9155 (s, 1H, H-1), 8.293 (d, 1H, H-3), 8.171 (t, 2H, H-2,4), 7.872 (t, 1H, H-5), 2.999 (m, 4H, CH_2-7,8), 1.481 (m, 6H, CH_3-9,10). FT-IR (cm^{-1}): 3057, 2971, 2885, 2288, 2254, 2209, 2146, 1646, 1408, 1389, 1325, 1151, 1028.

Table S1. The water content and bromide ion concentration and purity of the quinolizinium salts.

Salt	Water[a] (ppm)	Br ion[b] (wt%)	Purity[c]	Salt	Water[a] (ppm)	Br ion[b] (wt%)	Purity[c]
[MMQu]Br	302	33.8[d]	> 98%	[EEQu]Br	292	30.3[e]	> 98%
[MMQu]NTf_2	41	0.02	> 98%	[EEQu]NTf_2	35	0.04	> 98%
[MMQu]BF_4	150	0.15	> 98%	[EEQu]BF_4	138	0.14	> 98%
[MMQu]DCA	263	0.03	> 98%	[EEQu]DCA	233	0.02	> 98%

[a] Water content after vacuum drying at 80 °C and 10^{-2} ~ 10^{-3} mbar for 20 h. [b] Bromide ion concentration. [c] According to the observed experimental results: 1) there is no obvious impurity peak in ^{1}H-NMR, ^{13}C-NMR and ESI-MS spectra; 2) the Br ion concentration in Br-based salts agrees well with calculated value; 3) the Br ion concentration in Br-free compounds is no more than 0.15 wt%; and 4) the water content in these salts is no more than 302 ppm. [d] Calculated value = 33.6 %. [e] Calculated value = 30.6 %.

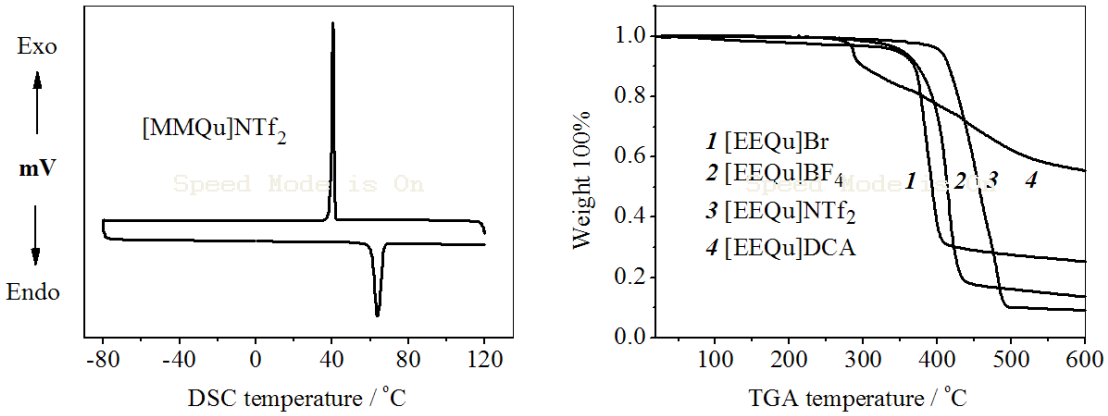


Fig. S1 Typical thermal analysis traces.

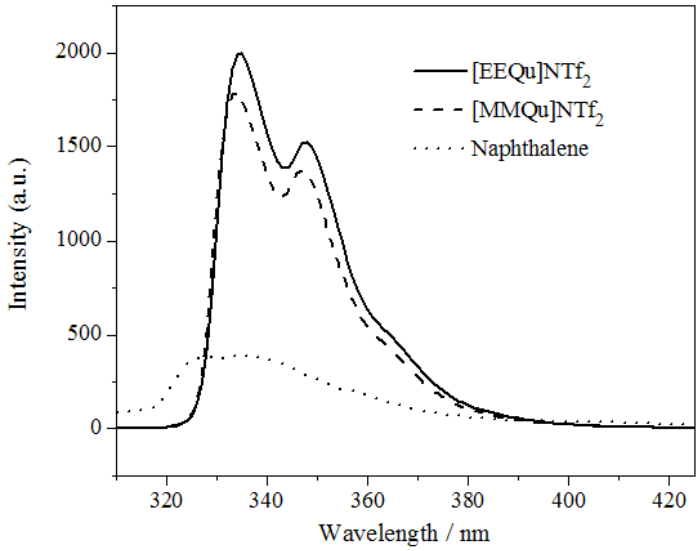


Fig. S2 Maximum emission spectra in 5×10^{-6} mol/L ethanol solution.

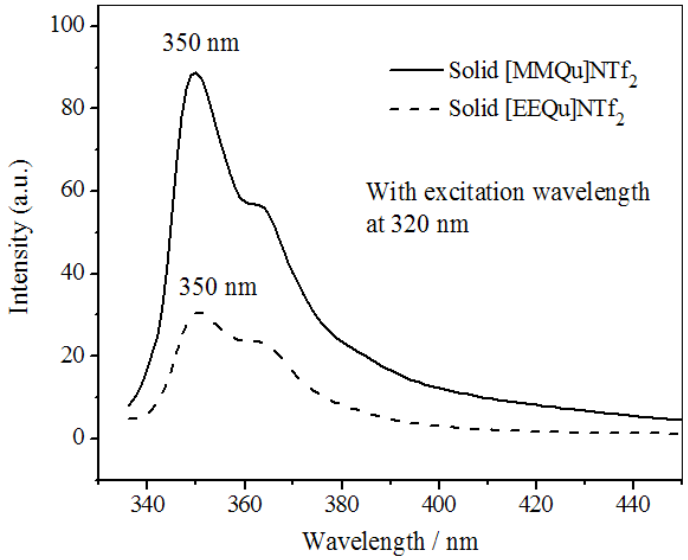


Fig. S3 Emission spectra in solid state.

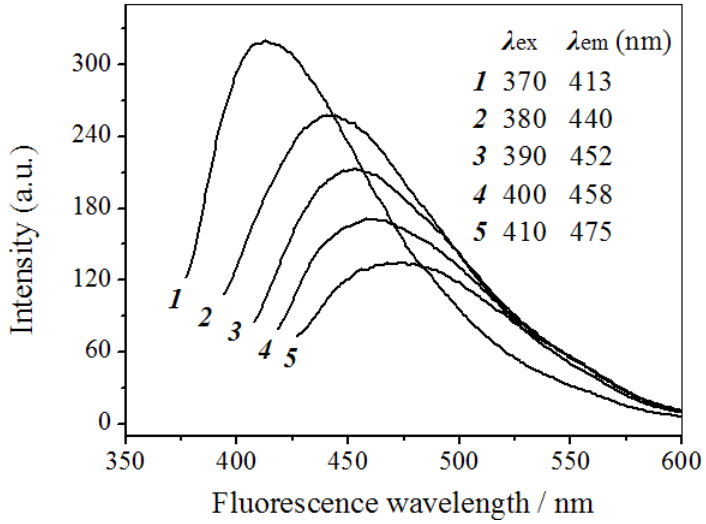


Fig. S4 Emission spectra of $[MMQu]NTf_2$ in liquid state at 60 ^{o}C.

Computational details

All calculations were performed using the Gaussian 03 program with the basis set in gas phase. The geometry of the ground-state [MMQu] cation was optimized without any constraint at the B3LYP 6-31+G(d,p) level. The first excited state geometry optimization was calculated starting with the ground-state optimized geometry at TD-DFT method with the 6-311++G(d,p) basis set.

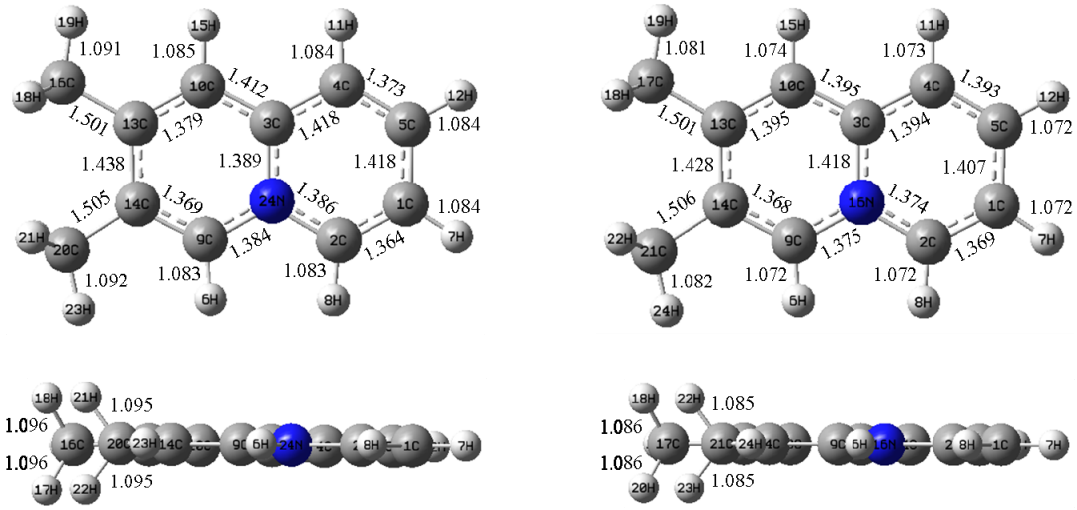


Fig. S5 The gas-phase-optimized geometries (bond length: Å) of [MMQu] for the ground state (left) and the first excited state (right).

Table S2. Atom coordinates and atom charges for [MMQu] at the ground state.

Center Number	Atomic Symbol	Coordinates (Angstroms) X	Y	Z	Mulliken Charges
1	C	3.12686600	-0.72005100	0.00030400	0.003585
2	C	1.92500800	-1.36469500	0.00030200	-0.032315
3	C	0.73928600	0.73241100	-0.00020400	0.388323
4	C	1.98936900	1.40123300	-0.00031600	-0.605492
5	C	3.16791600	0.69721500	-0.00005100	-0.108585
6	H	-0.38098000	-2.42041900	0.00021600	0.167227
7	H	4.03764900	-1.30757300	0.00057100	0.185483
8	H	1.82544300	-2.44261400	0.00055400	0.175514
9	C	-0.46994300	-1.34110800	-0.00007000	-0.129963
10	C	-0.50393800	1.40185900	-0.00019100	-0.143417
11	H	1.97911900	2.48543100	-0.00058900	0.176474
12	H	4.12081000	1.21497800	-0.00010700	0.183351
13	C	-1.70962200	0.73188700	-0.00013700	0.602608
14	C	-1.68268300	-0.70571600	-0.00023900	-0.260262
15	H	-0.47939500	2.48645300	-0.00005000	0.168220
16	C	-3.01342900	1.47622600	0.00059700	-0.392146
17	H	-3.61367700	1.21744000	-0.87906600	0.191103
18	H	-3.61285100	1.21787900	0.88091600	0.191175
19	H	-2.85539200	2.55594600	0.00023400	0.176511
20	C	-2.95062800	-1.51639700	-0.00024500	-0.698736
21	H	-3.56018800	-1.29013200	0.88104400	0.191257
22	H	-3.55996900	-1.28967500	-0.88161800	0.191233
23	H	-2.74181700	-2.58799500	-0.00053800	0.170974
24	N	0.73314800	-0.65670200	-0.00000900	0.207876

Sum of electrons transferred from the hydrogen atoms and methyl groups into the ring is -(∑H + C_{16} + C_{20}) = -1.07764e ≈ -1.08e.

Table S3. Atom coordinates and atom charges for [MMQu] at the first excited state.

Center Number	Atomic Symbol	Coordinates (Angstroms) X	Y	Z	Mulliken Charges
1	C	3.12481900	-0.72101900	0.00001200	-0.261308
2	C	1.91451200	-1.35992100	0.00001100	0.139577
3	C	0.74228200	0.75374300	-0.00000900	-0.230947
4	C	1.97932300	1.39740200	-0.00000800	-0.040893
5	C	3.17643700	0.68519700	0.00000200	-0.463114
6	H	-0.39322100	-2.40399100	-0.00001900	0.220884
7	H	4.01976300	-1.31160900	0.00002100	0.245070
8	H	1.82925400	-2.42856100	0.00001900	0.186947
9	C	-0.47061800	-1.33448200	0.00000000	-0.106268
10	C	-0.49365100	1.40145500	-0.00001900	-0.311871
11	H	1.98720000	2.47064800	-0.00001600	0.232498
12	H	4.11673500	1.19981300	0.00000300	0.229824
13	C	-1.71283100	0.72425500	-0.00002000	0.782412
14	C	-1.68461100	-0.70317300	-0.00001000	-0.257396
15	H	-0.48456600	2.47504700	-0.00002700	0.184308
16	N	0.73006100	-0.66387300	0.00000000	0.404492
17	C	-3.00963700	1.47979500	0.00003000	-0.368042
18	H	-3.60530400	1.23331900	0.87441300	0.187474
19	H	-2.83912700	2.54776300	-0.00008900	0.188606
20	H	-3.60549200	1.23314500	-0.87417300	0.187444
21	C	-2.94936100	-1.52059200	-0.00001000	-0.691460
22	H	-3.55170000	-1.30189400	0.87537200	0.189583
23	H	-3.55170400	-1.30189800	-0.87538800	0.189587
24	H	-2.73224200	-2.58063700	0.00000000	0.162594

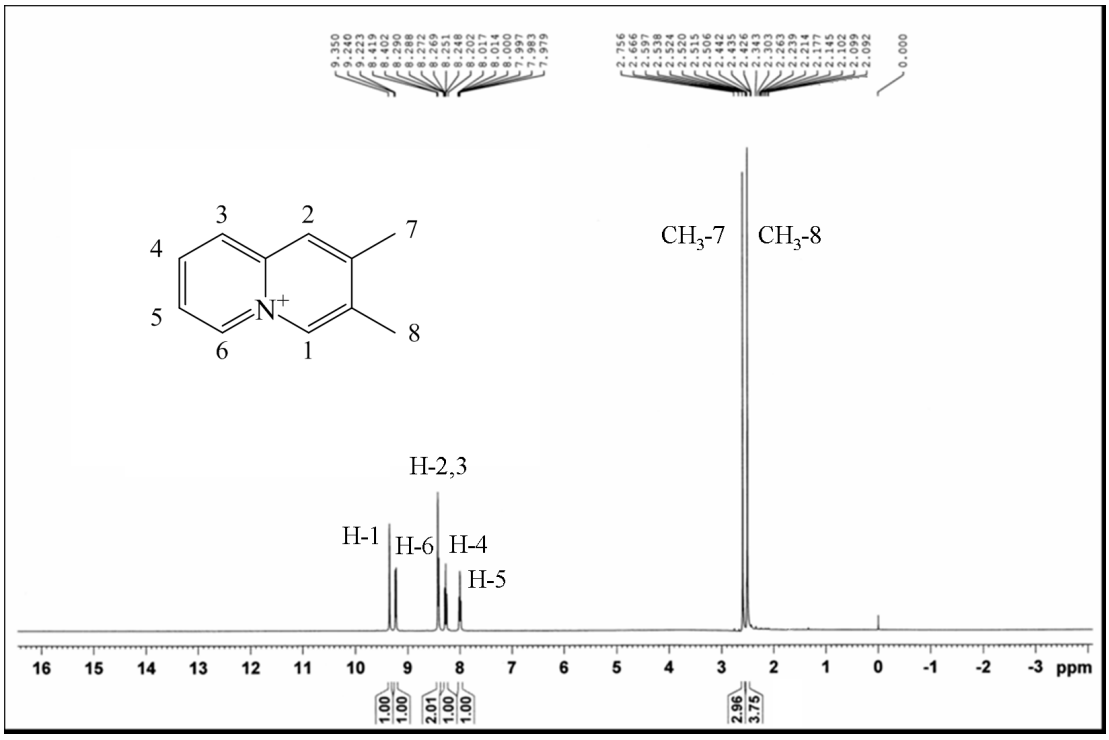


Fig. S6 ^{1}H-NMR of [MMQu]Br in DMSO.

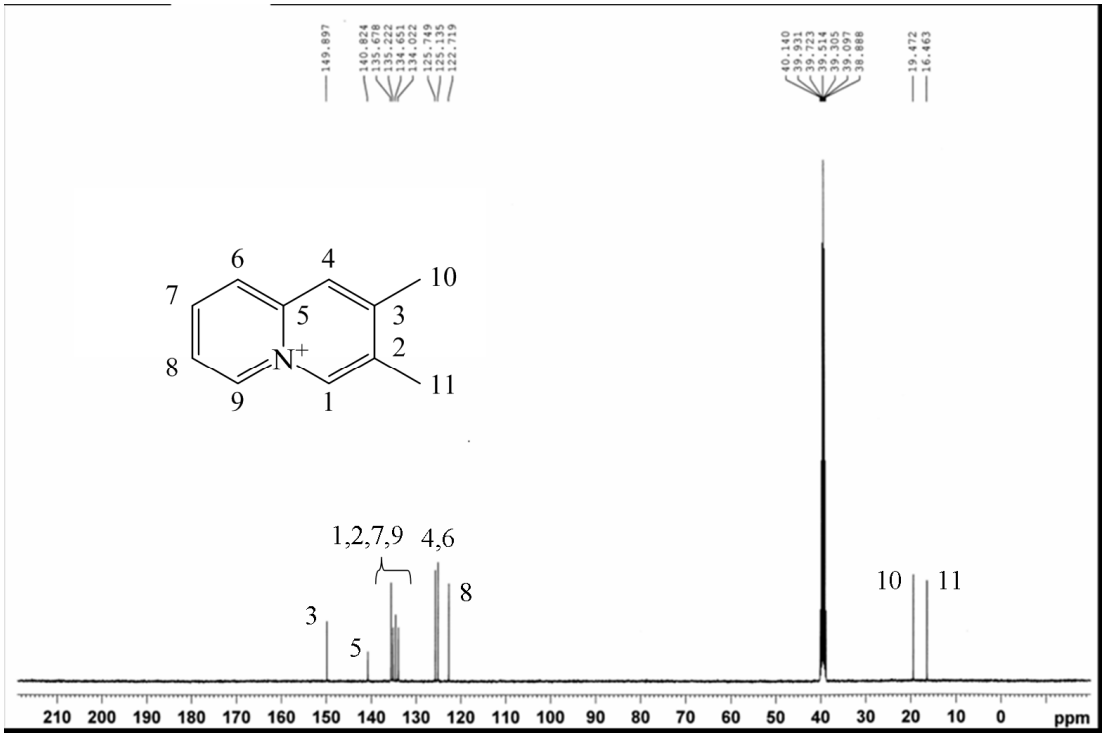


Fig. S7 ^{13}C-NMR of [MMQu]Br in DMSO.

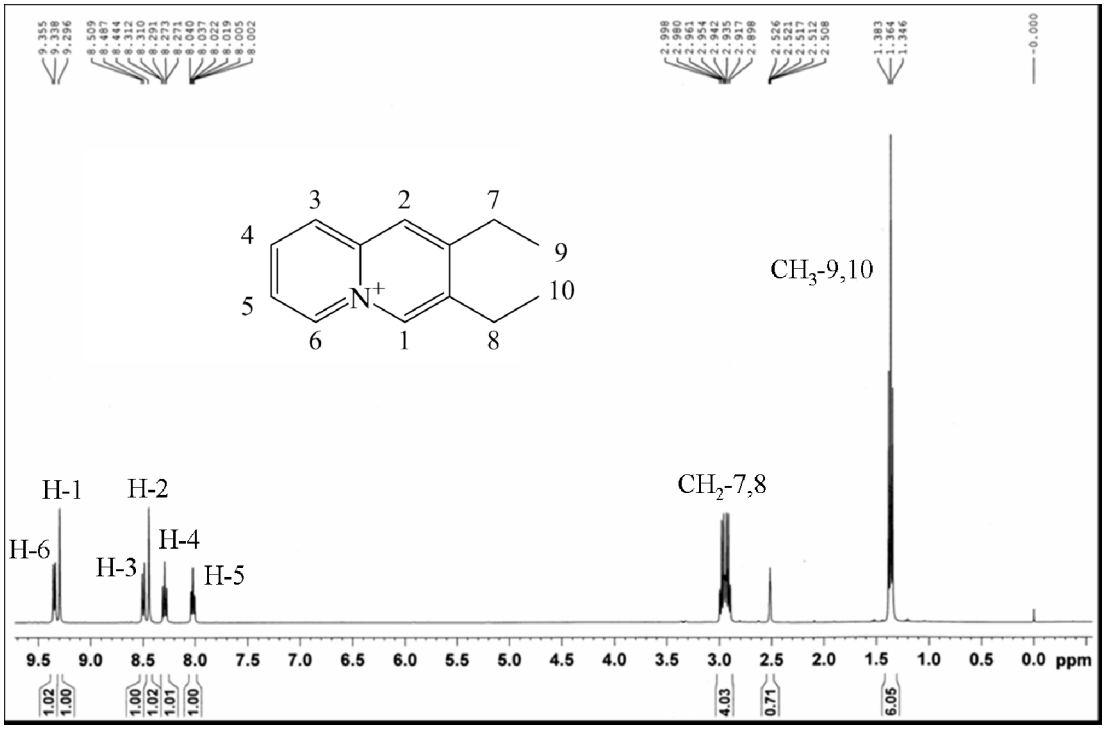


Fig. S8 ^{1}H-NMR of [EEQu]Br in DMSO.

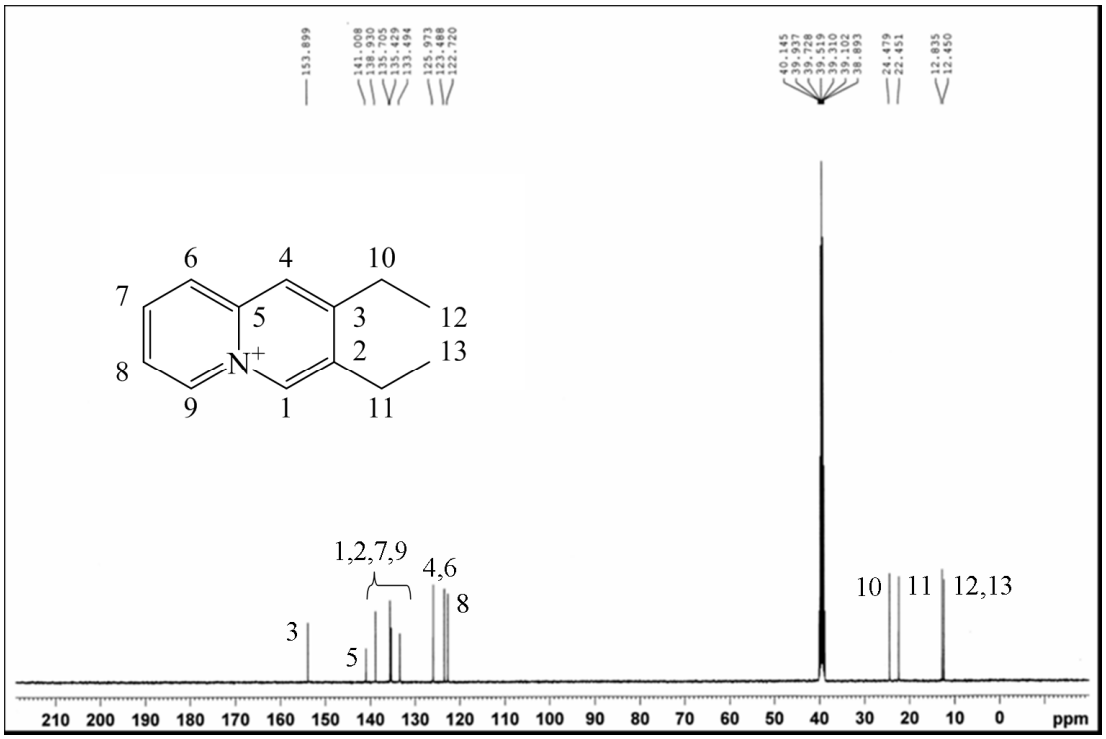


Fig. S9 ^{13}C-NMR of [EEQu]Br in DMSO.

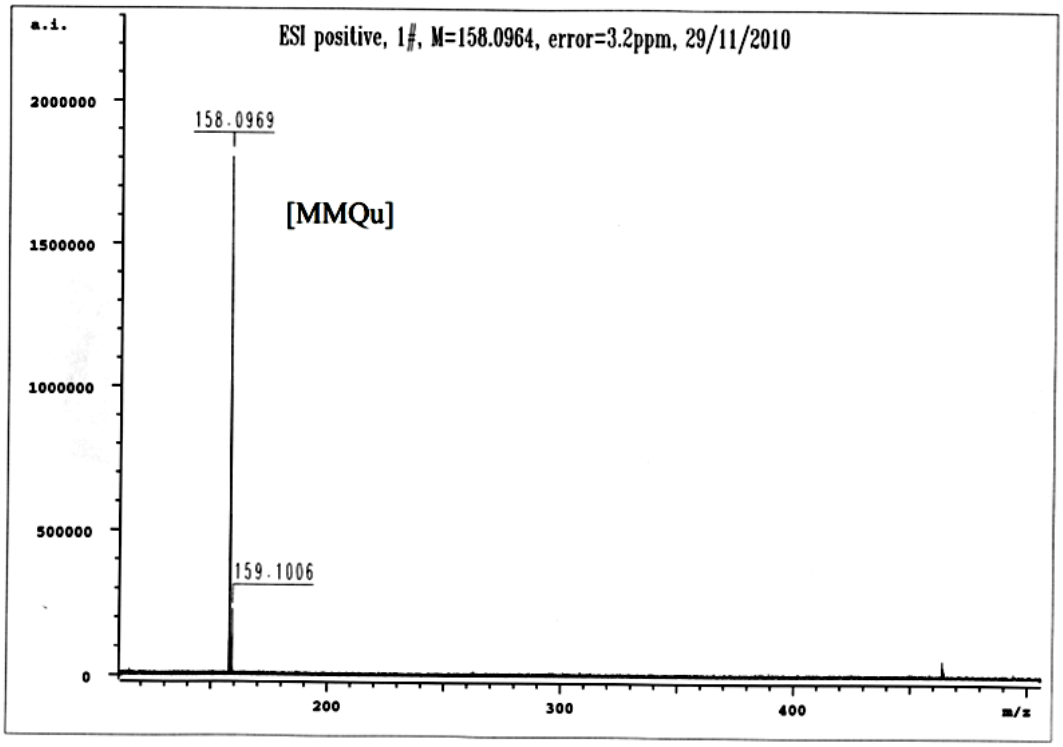


Fig. S10 ESI-MS of [MMQu]NTf_2.

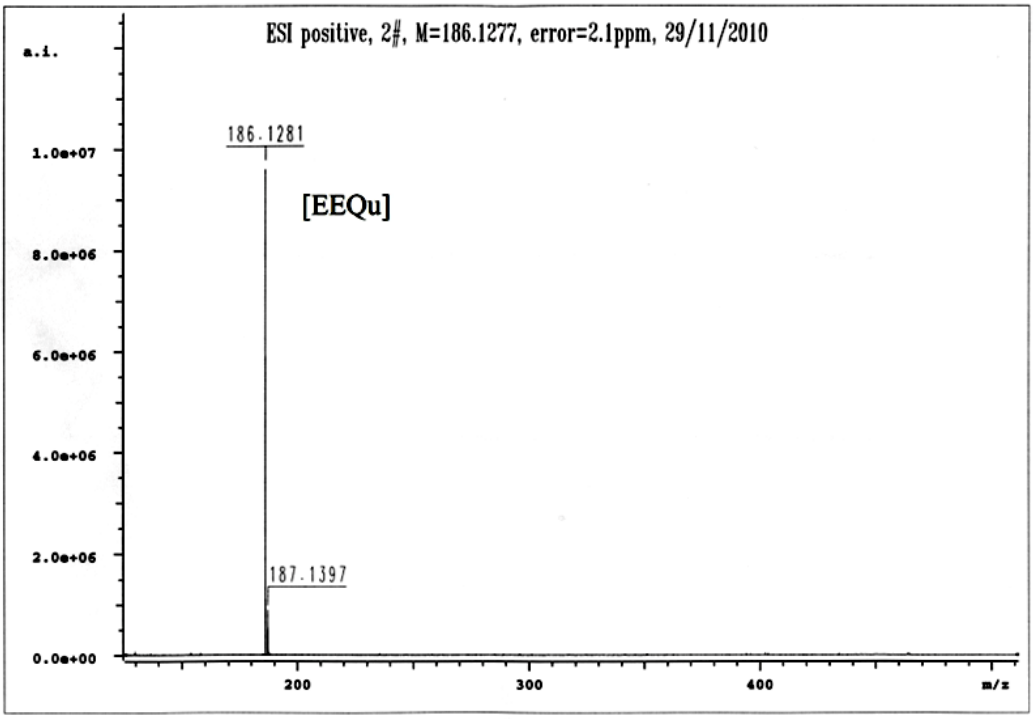


Fig. S11 ESI-MS of [EEQu]NTf_2.