2,6,10-Tris(dialkylamino)trioxatriangulenium salts: A new promising fluorophore. Ion-pair formation and aggregation in non-polar solvents

5 AUTHORS, INCLUDING:

Jóhannes Reynisson
University of Auckland
64 PUBLICATIONS   703 CITATIONS

SEE PROFILE

Kurt V Mikkelsen
University of Copenhagen
265 PUBLICATIONS   6,431 CITATIONS

SEE PROFILE

Niels Harrit
University of Copenhagen
28 PUBLICATIONS   836 CITATIONS

SEE PROFILE

Supplementary Information for

2,6,10-Tris(dialkylamino)-trioxatriangulenium salts - a new promising fluorophore. Ion-pair formation and aggregation in non-polar solvents

Bo W. Laursen*, Jóhannes Reynisson, Kurt V. Mikkelsen, Klaus Bechgaard and Niels Harrit*

Nano-Science Center and Department of Chemistry, University of Copenhagen, H.C. Oersted Ørsted Institute, Universitetsparken 5, DK-2100, Copenhagen, Denmark. E-mail: bwl@nano.ku.dk

15 pages
5 Figures

Experimental details

Syntheses of $(R_2N)_3TOTA^+$ with long alkyl chains

Methods and Materials. All reagents used were standard grade unless otherwise mentioned. NMR spectra were recorded on a 250 MHz Bruker spectrometer. Elemental analysis was done at the University of Copenhagen, Department of Chemistry, Elemental Analysis Laboratory, Universitetsparken 5, 2100 Copenhagen, Denmark.

The synthesis of compounds **1-Cl** and **1-BF$_4$** is described elsewhere.[1]

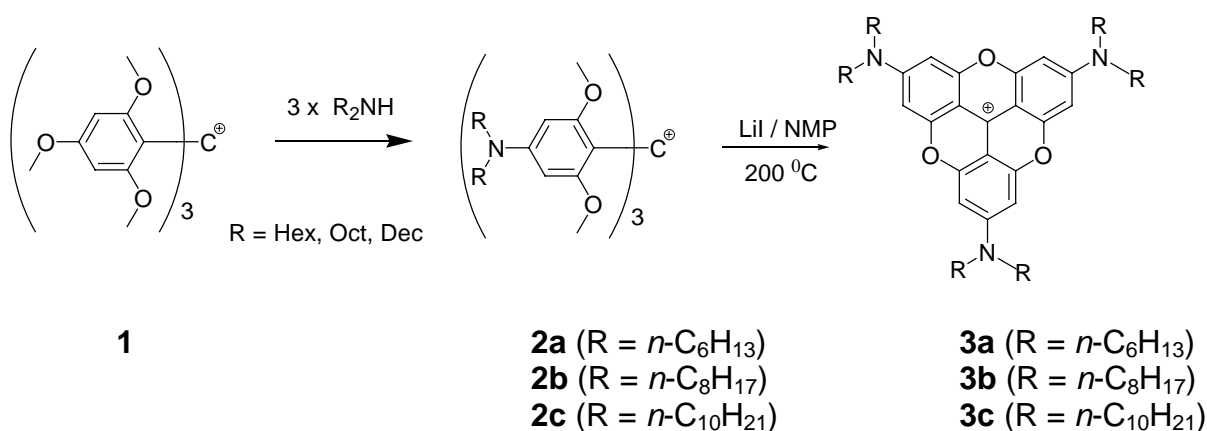| **1** | **2a** (R = n-C$_6$H$_{13}$) | **3a** (R = n-C$_6$H$_{13}$) |
| | **2b** (R = n-C$_8$H$_{17}$) | **3b** (R = n-C$_8$H$_{17}$) |
| | **2c** (R = n-C$_{10}$H$_{21}$) | **3c** (R = n-C$_{10}$H$_{21}$) |

Fig. S 1 Synthesis reaction scheme.

Substitution reactions were performed by reaction of tris(12,4,6-trimethoxyphenyl)carbenium salts (**1**) with excess of secondary amines, after the principles previously described.[1]

Tris(4-dihexylamino-2,6-dimethoxyphenyl)carbenium chloride (2a-Cl). Compound **1-Cl** (0.50 g, 0.9 mmol) was dissolved in purified DMF (10 mL) and dihexyl amine (10 g, 54 mmol) was added. The reaction mixture was kept at 60 °C for three days. The reaction mixture was absorbed on Silica (10 g) and washed thoroughly with diethyl ether. Purification by column chromatography on silica gel with ether/ethanol as eluent, yielded 0.25 g (27%) of a deep blue, sticky oil, which slowly crystallized. An identical compound was obtained in 38% yield by performing the reaction at room temperature over a period of

approximately two months. ^{1}H NMR (CDCl$_3$): δ 5.67 (6H, s), 3.49 (18H, s), 3.37 (12H, t, J = 7.6), 1.63 (12H, m), 1.31 (36H, m), 0.87 (18H, t, J = 6.5). MS (FAB[+]): m/z 973 (M[+]).

Tris(4-dioctylamino-2,6-dimethoxyphenyl)carbenium tetrafluoroborate (2b-BF$_4$). A solution of dioctyl amine (6 g, 25 mmol) in benzene (6 mL) was added to a solution of **1-BF$_4$** (0.5 g, 0.8 mmol) in NMP (5 mL). The reaction mixture was stirred under argon at 45 °C for four weeks. The reaction mixture was diluted with ether (100 mL) and silica (15 g) was added. The solvent was evaporated and the blue solid material was placed on a 2 cm layer of silica in a sieve. The solid was thoroughly eluded with petrolether and diethyl ether/petrolether (1:1) before the blue products was washed out with diethyl ether/CH$_2$Cl$_2$ (3:1, ca 400 mL). The solvent was evaporated and the blue oil redissolved in diethyl ether and washed with aqueous KPF$_6$ (0.1 M, 2x100 mL). Evaporation of the solvent and column purification (silica, petrolether/ethylacetate 3:1) gave the dark blue product in 24% yield (0.26 g). ^{1}H NMR (CDCl$_3$): δ 5.72 (6H, s), 3.53 (18H, s), 3.41 (12H, t, J = 7.5), 1.67 (12H, m), 1.34 (60H, m), 0.90 (18H, t J = 6.7). MS (MALDI-TOF): m/z 1140 (M[+]).

Tris(4-didecylamino-2,6-dimethoxyphenyl)carbenium tetrafluoroborate (2b-PF$_6$). A solution of didecyl amine (5 g, 17 mmol) in benzene (10 mL) was added to a solution of **1-BF$_4$** (0.5 g, 0.8 mmol) in NMP (10 mL). The inhomogeneous slurry was stirred under argon at 50 °C for three weeks. The reaction mixture was diluted with ether (100 mL) and silica (10 g) was added. The solvent was evaporated and the blue solid material was placed on a 2 cm layer of silica in a filter. The solid was thoroughly washed with petrolether before a light blue product was washed out with diethyl ether/petrolether (1:1, ca 400 mL). The solvent was evaporated and the blue oil redissolved in ether and washed with aqueous KPF$_6$ (0.1 M, 3x100 mL). Evaporation of the solvent and column purification (silica, petrolether/ethyl acetate 4:1) gave the blue sticky product in 20% yield (0.24 g). ^{1}H NMR (CDCl$_3$): δ 5.72 (6H, s), 3.55 (18H, s), 3.41 (12H, t, J = 7.3), 1.67 (12H, m), 1.29 (84H, m), 0.90 (18H, t, J = 6.5). ^{13}C NMR (CDCl$_3$): δ 163.56, 154.01, 115.39, 89.25, 56.31, 51.72, 32.27, 29.99, 29.93, 29.85, 29.69, 28.15, 27,45, 23.06, 14.49. MS (MALDI-TOF): m/z 1307 (M[+]).

Ring Closure. All the ring closure reactions were performed by heating the corresponding hexamethoxy compounds with anhydrous LiI in NMP as described previously.[1] However, improved yields were however obtained when the reactions were carried out in higher dilution and with higher concentration of LiI.

2,6,10-Tris(dihexylamino)-4,8,12-trioxatriangulenium hexafluorophosphate (3a-PF₆). **2a-Cl** (230 mg, 0.23 mmol) and LiI (0.35 g, 2.6 mmol) was heated to 160 °C in NMP under N_2 for 4 hours. Aqueous KPF_6 solution (0.2 M) was added, and the mixture was extracted with diethyl ether. The orange ether phase was washed with aqueous KPF_6 and the solvent evaporated. Column purification (silica, CH_2Cl_2/ether 1:1) and recrystallisation by slow evaporation of a dichloromethane/heptane solution, gave 65 mg (29%) of soft orange needles. Melting point (DSC, 10ºC/min): 143.4 - 145.3 ºC. ^{1}H NMR (250 MHz, CDCl₃): δ 6.30 (6H, s), 3.39 (12H, t, $J = 7.7$ Hz), 1.64 (12H, m), 1.37 (36H, m), 0.94 (18H, t $J = 6.5$ Hz). ^{13}C NMR (400 MHz, CDCl₃): δ 157.17, 154.81, 131.52, 95.22, 95.05, 52.69, 32.44, 27.81, 27.31, 23.49, 14.43. MS (FAB⁺) m/z: 834 (100%), 832 (30%), 776 (5%), 764 (20%), 748(15%), 678 (30%), 522 (10%), 366 (5%). UV-vis (CH_2Cl_2) λ_{max} (nm) (log ε): 476(5.19), 452(4.89 sh), 313(4.47), 303(4.34 sh). Anal. Calcd for $C_{55}H_{84}N_3O_3PF_6$: C, 67.39; H, 8.64; N, 4.29. Found: C, 67.23; H, 8.51; N, 4.30.

2,6,10-Tris(dihexylamino)-4,8,12-trioxatriangulenium tetrafluoroborate (3a-BF₄). This compound was synthesized in analogy to the PF_6 salt by using a KBF_4 solution in the workup procedure. The extraction was performed using dichloromethane. Recrystallisation from dichloromethane/heptane yielded 38 mg (32%) of soft, yellow-orange needles. Melting point (DSC) 10ºC/min: 152.6-155.8 ºC. The MS(FAB⁺), ^{1}H-NMR, ^{13}C-NMR and UV-vis spectra were identical with those of the PF_6 salt. Anal. Calcd for $C_{55}H_{84}N_3O_3BF_4$: C, 71.64; H, 9.18; N, 4.56. Found: C, 71.22; H, 8.94; N, 4.56.

2,6,10-Tris(dioctylamino)-4,8,12-trioxatriangulenium hexafluorophosphate (3b-PF₆). **2b-BF₄** (250 mg, 0.19 mmol) and LiI (0.30g, 2.2 mmol) were heated to 170 °C in NMP (25 mL) under argon for 90 minutes. Aqueous KPF_6 solution (0.2 M, 150 mL) was added,

and the mixture was extracted with ether (2x150 mL). The combined orange ether phase was washed with aqueous KPF_6 (0.2 M; 50 mL) and the solvent evaporated. Column purification (silica, ether) and recrystallisation from heptane solution, gave 230 mg (87%) of soft orange needles. Melting point (DSC) 10ºC/min: 110-114 ºC. ^{1}H NMR (400 MHz, CD_3CN): δ 6.33 (6H, s), 3.40 (12H, t, J = 7.7 Hz), 1.65 (12H, m), 1.35 (60H, m), 0.92 (18H, t J = 7.1 Hz). ^{13}C NMR (250 MHz, CD_3CN): δ 157.23, 154.92, 95.29, 95.15, 52.71, 32.69, 30.18, 30.15, 27.81, 27.63, 23.50, 14.52. MS (MALDI-TOF) m/z: 1003 (M^+). Anal. Calcd for $C_{67}H_{108}N_3O_3PF_6$: C, 70.06; H, 9.48; N, 3.66. Found: C, 69.61; H, 9.43; N, 3.66.

2,6,10-Tris(didecylamino)-4,8,12-trioxatriangulenium hexafluorophosphate ($3c$-PF_6).

Compound **2b-PF$_6$** (0.40 g, 0.27 mmol) and dry LiI (2.0 g, 15 mmol) was heated to 180 °C in NMP under argon for 60 minutes. After cooling the reaction mixture was poured into aqueous KPF_6 solution (0.2 M), and the solution extracted with ether (3x100 mL). The ether phase was washed with aqueous KPF_6 and the solvent evaporated. Column purification (silica, petrolether/ethyl acetate 4:1) and recrystallisation from heptane (cooled to −20 °C), gave 0.20 g (56%) of soft orange needles. ^{1}H NMR ($CDCl_3$): δ 6.48 (6H, s), 3.46 (12H, t, J = 7.7 Hz), 1.71 (12H, m), 1.35 (84H, m), 0.91 (18H, t J = 6.5 Hz). ^{13}C NMR ($CDCl_3$): δ 156.01, 153.99, 131.20, 94.63, 52.23, 31.77, 29.48, 29.42, 29.32, 29.18, 26.99, 26.89, 22.56, 14.00. MS (MALDI-TOF): m/z 1171 (M^+). Anal. Calcd for $C_{79}H_{132}N_3O_3PF_6$: C, 72.05; H, 10.10; N, 3.19. Found: C, 71.77; H, 10.11; N, 3.17.

Photophysical measurements

Benzene and CH_2Cl_2 (Labscan, Analytical Science) and other reagents were used as received.

Absorption spectra were measured on a Perkin-Elmer Lambda 17 UV/VIS spectro-photometer with 0.5 nm resolution. Usually 1x1 cm optical quartz cells were used, but in experiments investigating the effects of concentration (*e.g.* Fig.5) the path length was varied in a reciprocal relationship with concentration. Absorption coefficients were determined by measuring an aliquot from a stock solution (CH_2Cl_2) into a volumetric flask.

CH_2Cl_2 was removed in a stream of argon and solvent (CH_2Cl_2, benzene, heptane, or dibutyl ether) was added to the mark.

Steady state and time-resolved fluorescence experiments were performed in the normal 90° configuration with a standard 1x1 cm optical quartz cell. The concentration of $(R_2N)_3$-$TOTA^+$ PF_6^- was ca. 1.0×10^{-5} M or less in all fluorescence experiments. All the experiments were performed at 20 °C. For steady state fluorescence emission spectra the LS-50B instrument from Perkin-Elmer was used with 2.5 nm resolution unless specified otherwise.

Coumarin 153 in EtOH was used as reference for fluorescence quantum yield determinations. Its has been reported to have a quantum yield of 0,38.[2] To assure that the reported value is correct, the quantum yield in this solvent was measured against quinine bisulphate in air saturated 1 N H_2SO_4, $\Phi_f = 0.55$[3] The value thus found for coumarin 153 was 0.36 ± 0.05, thus in very good agreement with the literature value. Solutions were optically dilute in order to prevent inner filter effects. Emission spectra were corrected and intensities were corrected for refraction index.[4] $(R_2N)_3$-$TOTA^+$ samples were purged with argon prior to measurements.

Fluorescence lifetimes were measured on a time-correlated single-photon-counting (SPC) apparatus (FL900, Edinburgh Analytical Instruments) equipped with a Hamamatsu R1527 photomultiplier and a nitrogen filled nanosecond flash lamp. The nitrogen lines at 337 nm and 407 nm were used for excitation. Emission was detected at 520 nm. All samples were purged with argon prior to measurements. A Ludox dispersion was used to obtain the instrument response function. Fluorescence decay curve analysis was performed by reconvolution of the instrument response function with an assumed decay law. The decay parameters were determined by a least-squares fitting routine, the quality of which was evaluated by the reduced χ^2 values, as well as by the randomness of the weighted residuals.

Table S 1. Photophysical data for $(Hex_2N)_3\text{-}TOTA^+PF_6^-$ and $(Oct_2N)_3\text{-}TOTA^+PF_6^-$

R	Solvent	λ_{max}^{ABS} (nm) (ε ($M^{-1}cm^{-1}$))	λ_{max}^{FLU} (nm)	Stokes' shift (cm^{-1})	Quantum Yield[a] ϕ_f	Lifetime τ_f (ns)	Radiative Lifetime $\tau_0 = \tau_f/\Phi_f$
Hex	CH$_2$Cl$_2$	476 (156000)		b	b	b	b
	Benzene	455 (94100) 492 (98200)		b	b	b	b
	Heptane	458 (100300)		b	b	b	b
Oct	CH$_2$Cl$_2$	476 (153000)	496	936	0.73	3.5	4.8
	Benzene	455 (97000) 492 (102000)	516	945	0.55	3.0	5.5
	Heptane	459 (94000)	545	2774	0.16	$\tau_1 = 3.1$ (36%) $\tau_2 = 23.6$ (64%)[c]	$\tau_2/\phi_f =$ 147

a) The value for $(Oct_2N)_3\text{-}TOTA^+PF_6^-$ was determined relative to coumarin 153 in EtOH. The value for $(Hex_2N)_3\text{-}TOTA^+PF_6^-$ was determined relative to the value for $(Oct_2N)_3\text{-}TOTA^+PF_6^-$.

b) Value not determined.

c) The distribution of lifetimes was invariant with concentration in the range from 5.5×10^{-5} to 1.2×10^{-6} M.

Calculations

Molecular structure of the free cation

Three methods were used to calculate the structure of the free $(Me_2N)_3$-TOTA$^+$ ion: 1) Two semi empirical methods (AM1 and PM3) and, 2) a DFT calculation (B3LYP/6-31G(D)). The structures calculated are compared the X-ray crystal structures of the closely related compound [Pyr$_3$-TOTA$^+$][PF$_6^-$] (Fig. S 2). Table S 2 lists selected bond lengths obtained by the semi empirical and the DFT calculations along with the crystal values.
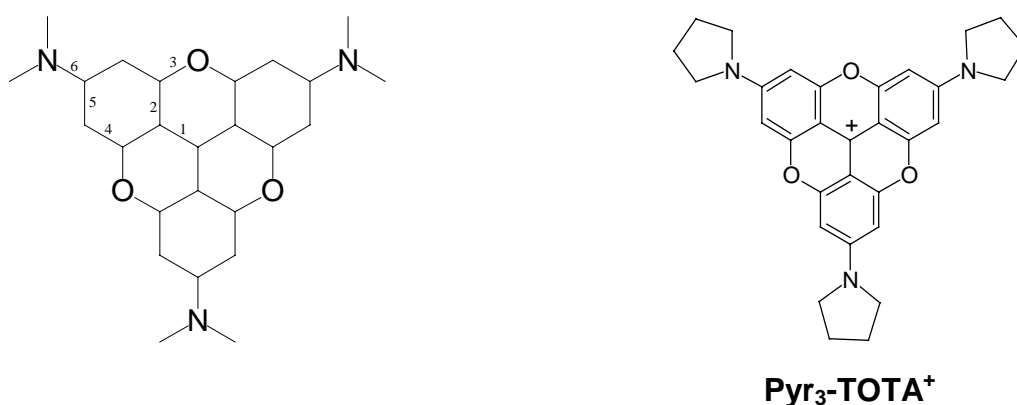

Pyr$_3$-TOTA$^+$

Fig. S 2. Structure and bond numbering of the model system, tris(dimethylamino)-trioxatriangulenium ion and the pyrrolidinyl analog for which a crystal structure is known.[1]

Table S 2. Calculated bond lengths (Å) vs. X-ray values

Bonds[a]	AM1	PM3	DFT	X-ray[b]	ΔAM1[c]	ΔPM3[c]	ΔDFT[c]
1	1.397	1.396	1.392	1.392	0.005	0.004	0.000
2	1.415	1.415	1.409	1.401	0.014	0.014	0.008
3	1.394	1.387	1.379	1.390	0.004	-0.003	-0.011
4	1.383	1.383	1.377	1.368	0.015	0.015	0.009
5	1.437	1.427	1.431	1.430	0.007	-0.003	0.001
6	1.371	1.388	1.363	1.344	0.027	0.044	0.019
				rms:	0.012	0.014	0.008

a) As defined in Fig. S 2.

b) Data taken from the X-ray structure of [Pyr$_3$TOTA$^+$][PF$_6$]. Bond lengths averaged in accordance with the assumed D_{3h} symmetry of the molecule.

c) Deviation from the averaged X-ray structure.

All three methods do generate structures with the expected D_{3h} symmetry that match the crystal structure quite well. For most bond lengths the deviation is comparable to the accuracy of the crystal structure *i.e.* less than 0.010 Å.

Ion-pair structure

Structures of the [(Me$_2$N)$_3$-TOTA$^+$][PF$_6^-$] ion pair were optimised using the semi empirical method AM1 in the program *Spartan*. A PF$_6^-$ ion (molecular mechanics optimised) was placed in ten different starting positions around the D_{3h} symmetric (Me$_2$N)$_3$-TOTA$^+$ ion. These positions are shown in Fig. S 3. The ten ion pair structures were geometry optimised by AM1, with no constrains. The geometry optimisation lead to six new minimized structures as shown in Fig. S 4 (Table S 3, Table S 4,Fig. S 5).

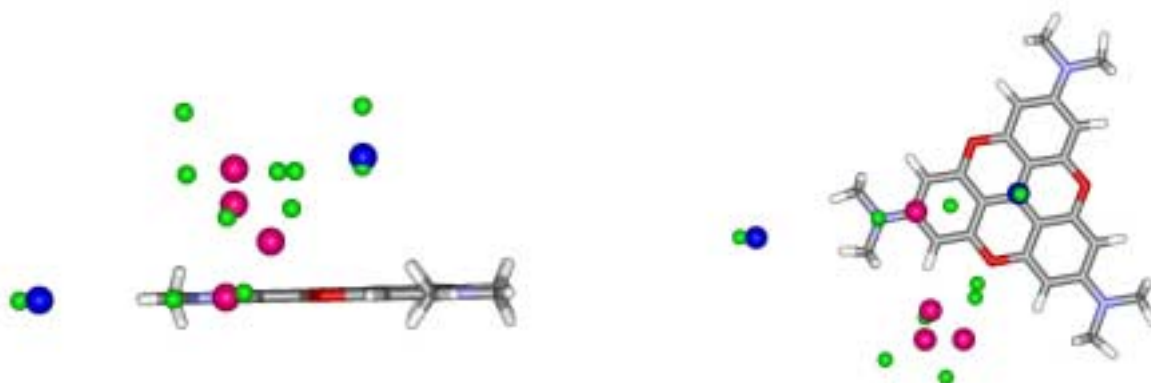Fig. S 3. Starting positions for optimisation of ion-pair structure viewed from the side and from the top.

Fig. S 4. 3D representation of the relative location of the PF_6^- ion in the optimised structures of $[(Me_2N)_3\text{-}TOTA^+][PF_6^-]$; PF_6^- starting positions (green); Optimised structures **H1** and **H2** are blue, and **M1**-**M4** are shown in red**.**

Table S 3. Calculated (AM1) relative formation energies and characteristic distances within the geometry optimised ion pair structures of $[(Me_2N)_3\text{-}TOTA^+][PF_6^-]$

Ion pair structure	Energy[a] (kJ/mol)	Distance from P to the plane of the cation (Å)	Distance from P to the central atom in the cation (Å)	Distances from P to the three nitrogen atoms (Å)
M1	6	4.13	6.17	4.27
				9.59
				9.59
M2	0	1.31	6.53	6.11
				6.11
				12.05
M3	4	0.00	6.86	5.16
				7.36
				12.36
M4	6	2.28	6.99	5.22
				7.70
				12.29
H1	17	4.4	4.36	6.84
H2	23	0.00	10.62	5.08
				14.25
				14.25

a) Relative to ion pair **M2**

Table S 4. Selected bond lengths in the cationic moiety of the optimised ion pair structures

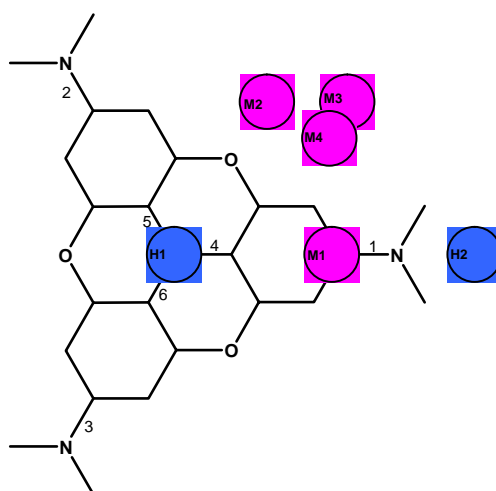| Bond[a]	Free cation D_{3h} (AM1)	M1	M2	M3	M4	H1	H2
1	1.371	1.365	1.372	1.366	1.366	1.382	1.353
2	-	1.380	-	1.375	1.375	-	1.377
3	-	-	1.379	1.379	1.379	-	-
4	1.397	1.383	1.393	1.387	1.387	1.399	1.383
5	-	1.404	-	1.398	1.398	-	1.404
6	-	-	1.405	1.405	1.405	-	-

a) See Fig. S 5.

Fig. S 5. Schematic representation of the location of the PF_6^- ion in the optimised ion pairs. Selected bonds are numbered 1-6 (see Table S 4).

Dipole Moments of Ion-pairs

Table S 5. Calculated (ZINDO) dipole moments of the S_0, S_1, and S_2 states in ion pairs **M1** − **M4** and **H1-H2**.

Ion-pair geometry	μ (S_0) (D)	μ (S_1) (D)	μ (S_2) (D)
M1	24	20	27
M2	25	20	30
M3	27	21	31
M4	28	23	32
H1	16	17	17
sH2	44	38	50

Spectral Calculations for a Possible Dimer

The model dimer was constructed by placing two **M2** ion pairs in a cofacial-staggered conformation, with an inter-plane distance of 3.5 Å, and the two PF_6^- ions antiparallel above and below the plane of the dimer. Without any structure optimisation a spectral ZINDO-CI calculation was performed. Single excitations involving the 60 highest occupied and 60 lowest unoccupied molecular orbitals were included in the configuration interaction calculations. The calculated transition energies and oscillator strengths are listed in Table S 6.

Table S 6. Calculated transition energies and oscillator strengths of ground and excited states in a model dimer

State	Energy (cm^{-1})	OS	μ (D)
Ground	0	-	2.4
1	21780	0.01	1.8
2	22520	0.03	4.1
3	23450	1.3	3.2
4	23620	1.0	2.0

References in Supplementary Material

1   B. W. Laursen, F. C. Krebs, M. F. Nielsen, K. Bechgaard, J. B. Christensen and N. Harrit, 2,6,10-Tris(dialkylamino)-triangulenium Ions. Synthesis, Structure, and Properties of Exceptionally Stable Carbenium Ions, *J. Am. Chem. Soc.*, 1998, **120**, 12255.

2   G. Jones II, W. R. Jackson, C.-Y. Chio and W. R. Bergmark, Solvent Effects on Emission Yield and Lifetime for Coumarin Laser Dyes. Requirements for a Rotary Decay Mechanism., *J. Phys. Chem.*, 1961, **65**, 229.

3   D. F. Eaton, Reference Materials for Fluorescence Measurement, *Pure Appl. Chem.*, 1988, **60**, 1107.

4   D. F. Eaton, Luminescence Spectroscopy, in *Handbook of Organic Photochemistry*, ed.Scaiano, J. C., CRC Press, Boca Raton, Florida, 1989, p. 231.