SUPPLEMENTARY MATERIAL FOR
PPS B20495F

1 Experimental details

Trioxatriangulenium (4,8,12-trioxadibenzo[*cd,mn*]pyrenylium) tetrafluoroborate was synthesized from the carbinol by reaction with HBF_4.[1,2] Methanol and acetonitrile (Labscan, Analytical Science) and other reagents were used as received. The water used as solvent was triply distilled.

Absorption spectra were measured on a Perkin-Elmer Lambda 5 UV/VIS spectrophotometer with 1 nm resolution in 1x1 cm optical quartz cells. Absorption coefficients were determined by measuring an aliquot from a stock solution (acetonitrile) into a volumetric flask. Acetonitrile was removed in a stream of argon and solvent (methanol, ethanol, water, or acetonitrile) 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 $TOTA^+$ 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 FS900 instrument from Edinburgh Analytical Instruments was used with 1.8 nm resolution.

Quinine bisulphate in air saturated 1 N H_2SO_4, $\Phi_f = 0.55$ [3] was used as reference for fluorescence quantum yield determination. Sample ($TOTA^+$) and reference solutions were excited at 320 nm, where they had identical absorbance. Solutions were optically dilute in order to prevent inner filter effects. Emission spectra were uncorrected, but $TOTA^+$ and quinine sulphate fluoresce in the same spectral range, so the error introduced from any wavelength dependent response of the fluorometer is considered negligible. Emission intensities were corrected for variation in refraction index.[4] $TOTA^+$ 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.

In the laser flash photolysis experiments a quartz cell of the proportions 25 mm long, 9 mm wide and 20 mm tall was used. It was connected to a solution reservoir by an airtight glass tubing. The solutions were purged with argon prior to irradiation for at least 20 min. Solutions of $TOTA^+$ were prepared in acetonitrile or triply distilled water with $A_{308} = 0.600$ ($[TOTA^+] = 1\times10^{-4}$ M). In both cases, 20 μL of 48% wt. tetrafluoroboric acid solution in water (Aldrich) was added to the $TOTA^+$ solutions (100 mL). Samples were irradiated by means of a Lambda Physik EMG102 xenon-chloride laser with excitation wavelength at λ = 308 nm. The laser pulse had duration of ca. 10 ns and an energy output of approximately 0.8 J/pulse. The monitoring system consisted of a xenon lamp (VIX-150 UV) and a lamp pulser (custom built). The xenon lamp generated a continuum of light from 200 nm to 900 nm and was pulsed for ca. 4 ms, temporarily increasing the current, to generate intense monitoring light. UniBlitz (model D122) shutters controlled the passage of monitoring light through the sample and the excitation beam from the laser. The detection system consisted of a monochromator (2035 McPherson, 0.35-meter scanning monochromator) and a photomultiplier (PHM 1P28). A Stanford DG353 four-channel digital delay/pulse generator was used to trigger the laser and the xenon lamp. The analog signal from the photomultiplier was sent to a LeCroy 940 dual 350 MHz oscilloscope where it was digitised and sent to a PC where the data was processed in a custom made program.

The phosphorescence spectrum of $TOTA^+$ was recorded at 77K on an LS-50B Perkin-Elmer luminescence spectrometer using the phosphorescence accessory. $TOTA^+$ was dissolved in ethanol (1.3×10^{-4} M) and irradiated in a 2 mm quartz tube submerged in liquid nitrogen.

^{1}H-NMR spectra were recorded on a Varian 400 MHz instrument using tetramethyl-silane (TMS) as internal standard. The deuterated solvents were used as received.

References

1 J. C. Martin and R. G. Smith, Factors Influencing the Basicities of Triarylcarbinols. The Synthesis of Sesquixanthydrol, *J. Am. Chem. Soc.*, 1964, **86** 2252.

2 F. C. Krebs, B. W. Laursen, I. Johannsen, A. Faldt, K. Bechgaard, C. S. Jacobsen, N. Thorup and K. Boubekeur, The geometry and structural properties of the 4,8,12-Trioxa-4,8,12,12C-tetrahydrobenzo[cd,mn]pyrene system in the cationic state. Structures of a planar organic cation with various monovalent and divalent anions, *Acta Cryst.*, 1999, **B55** 410.

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.

2 Supplementary figures

(Fig. 1s around here)

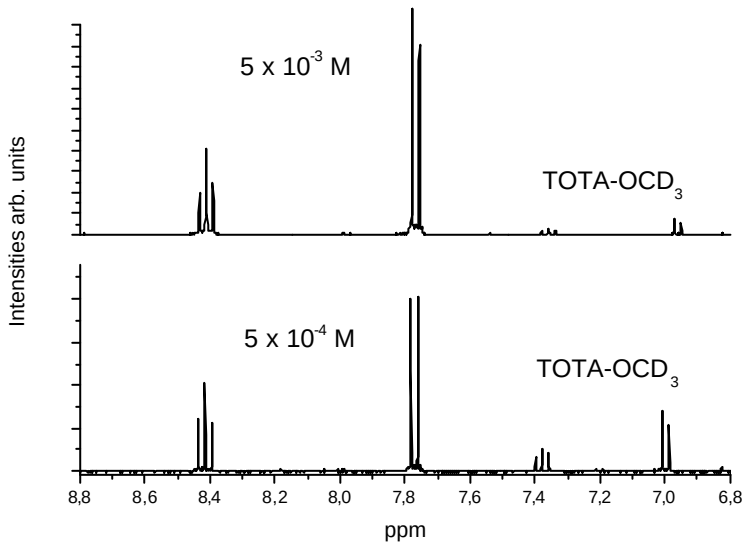

Fig. 1s ^{1}H-NMR spectrum of $TOTA^{+}$ BF_4^{-} in CD_3OD.

(Fig. 2s around here)

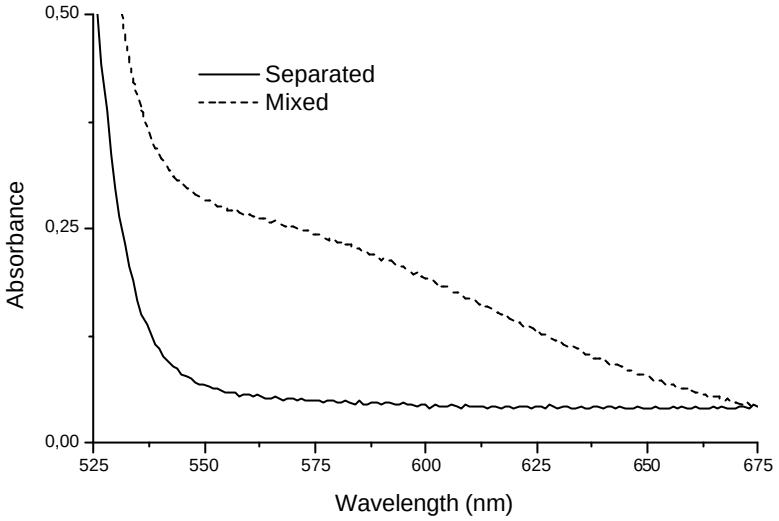

Fig. 2s Electronic absorption spectra of $TOTA^+$ and anthracene in concentrated acetonitrile solutions recorded in a 1 × 1 cm quartz tandem cell, first in separated compartments and then mixed together.

(Fig. 3s around here)

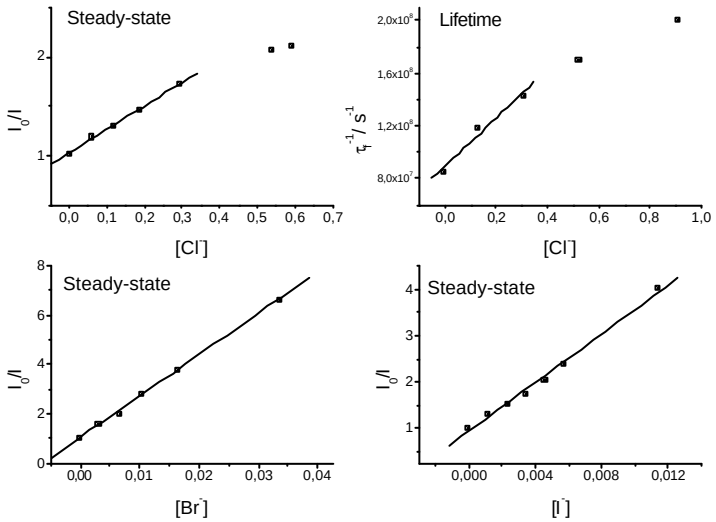

Fig. 3s Stern-Volmer plots for steady state quenching of TOTA+ fluorescence in water by [Cl^-] (top left), [Br^-] (bottom left), and [I^-](bottom right). Stern-Volmer plot for lifetime quenching $TOTA^+$ fluorescence in water by [Cl^-] (top right).