– Supporting Information –

Electron transfer across a spiro link: extreme solvatofluorochromism of a compact spiro-bridged N,N-dimethylaniline-phthalide dyad

Jerzy Karpiuk,[a]* Paweł Gawryś,[a] Elena Karpiuk[a] and Kinga Suwińska[b]

a) Institute of Physics, Polish Academy of Science, Al. Lotników 32/46, 02-668 Warsaw, Poland

b) Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University in Warsaw, K. Wóycickiego 1/3, 01-938 Warsaw, Poland.

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* Corresponding author, jkarpiuk@ifpan.edu.pl

S1   General experimental details

Synthesis and characterisation

5-amino-1-indanone (Manchester Organics) was used as received. All other reagents used in syntheses were purchased commercially and, except for tetrahydrofuran (THF), were used as received. THF for organometallic reactions was distilled under argon over CaH_2 prior to use.

TLC analysis was carried out using Merck Silica gel 60 F_{254} TLC plates and spots were visualised under UV light (365 or 254 nm). Silica gel column chromatography was performed with short 1 inch diameter columns packed with Silica gel 60 (Merck) suspended in hexane.

^{1}H and ^{13}C NMR spectra were recorded with Varian VNMRS 500 MHz or Bruker DRX 500 MHz spectrometers. ^{1}H NMR and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz, respectively. Residual solvent peaks were accounted for as described in the literature.[1] All chemical shifts are quoted in ppm and all coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used in reporting the multiplicity for NMR resonances: s = singlet, d = doublet, and m = multiplet. Samples were prepared using $CDCl_3$ (Merck).

Mass spectra (HRMS (EI+)) were obtained with a Waters AutoSpecPremier mass spectrometer.

Elemental analysis was conducted with an Elementar Vario EL III analyzer.

Melting points were obtained with an A. KRÜSS Optronic KSP1N melting point meter.

Photophysics

Solvents: n-hexane (HEX), cyclohexane (CHX), diethyl ether (EE, inhibitor free), methyl-*tert*-butyl ether (MTBE), ethyl acetate (EA), tetrahydrofuran (THF), dichloromethane (DCM) and acetonitrile (ACN), were all of spectroscopic grade, were purchased from Merck and used as received. Dibutyl ether (BE, anhydrous), diisopropyl ether (IPE, reagent grade), butyl acetate (BA, for HPLC), 1,2-dimethoxyethane (DME, for HPLC), and 1,2-dichloroethane (DCE, for HPLC) were purchased from Aldrich and used as received. Butyronitrile (BTN, Merck, for synthesis) was twice distilled over $KMnO_4 + K_2CO_3$ and P_2O_5. Propionitrile (PRN, Merck, for synthesis) was triply distilled over $KMnO_4 + K_2CO_3$, P_2O_5 and CaH_2.

The dielectric constant, ε, for PRN:BTN, 4:5, v/v mixture was calculated as the weighted average of the mixture components, assuming ideal solvent mixture and additive function of

solvent concentrations: $\varepsilon_{mix} = a_1\varepsilon_1 + a_2\varepsilon_2$, where a_i is a volume fraction of i-th solvent, and ε_i is its dielectric constant in the pure state (excess ε was neglected).[2]

Absorption spectra were recorded with Shimadzu UV-2700 spectrophotometer.

Steady-state fluorescence spectra were recorded using a Fluorolog-3 spectrofluorometer (Horiba-Jobin Yvon) equipped with a 450 W xenon CW lamp, as a number of quanta per unit wavelength. The fluorescence spectra were subsequently corrected for spectral response of the detection systems and additionally by subtraction of the background due to the solvent (e.g., Raman lines, reminders of the second order of the excitation line). The fluorescence spectra were recorded as a function of wavelength and subsequently multiplied by a factor λ^2 to convert counts per wavelength into counts per wavenumber. All luminescence measurements were carried out using solutions deoxygenated by saturation with analytically pure argon (typically for 30 minutes before measurement). The fluorescence quantum yields were determined using quinine sulfate in 0.1 N H_2SO_4 as a standard (Φ_f=0.51[3]) and corrected for the refractive index of a solvent.[4] For quantum yield determinations, optical density of both the sample and the standard were identical at the wavelength of excitation, and were of the order 0.05 - 0.15.

Fluorescence decays were recorded with Fluorolog-3 accessory for time-correlated single-photon counting (TC SPC) including a Delta Hub timing electronics and a DeltaDiode excitation source (303 nm), and analyzed using the DAS6 decay analysis software package provided by Horiba Jobin Yvon (practical time resolution 0.2 ns).

Calculations

The calculations were performed using a TURBOMOLE program package.[5]-[6] The ground state (S_0) equilibrium geometry of MGLA and MGLA-C5 were optimized using the MP2 method at the MP2/cc-pVDZ level of theory. The ground state dipole moments were calculated for the MP2/cc-pVDZ S_0 optimized geometries. The dipole moment calculated for MGLA (5.2 D) is slightly higher than the previously reported estimate (4.2 D) obtained with molecular mechanics calculations.[13] The HOMO and LUMO orbitals were calculated for the S_0 optimized geometries at the CC2-cc-pVDZ level of theory.

S2   Synthesis and characterisation

Methylation of 5-AI (5-amino-1-indanone) to 5-DMAI (5-(dimethylamino)-1-indanone)
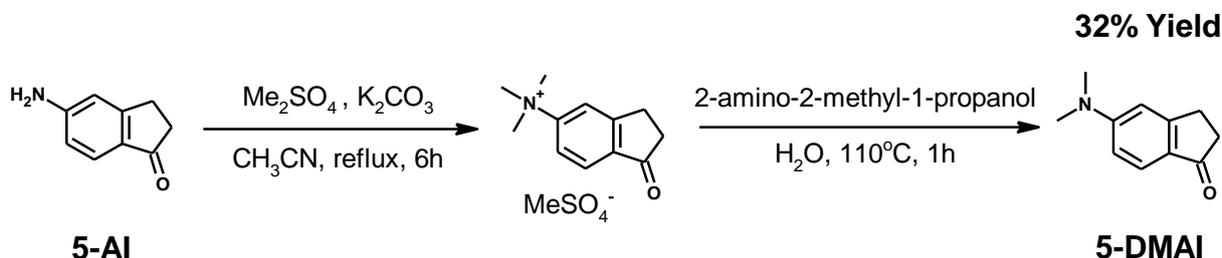
The reaction was carried out with no special protection against atmospheric oxygen or moisture. A stirred mixture of 5-amino-1-indanone (1.47 g, 10 mmol), potassium carbonate (powdered, 4.14 g, 30 mmol; 3 eq.), dimethyl sulphate (3.2 ml, 4.26 g, 33 mmol; 3.3 eq.) in acetonitrile (40 ml) was refluxed for 6 hours in a three-necked round bottom flask (100 ml), then allowed to cool down to 50°C and diluted with ethyl acetate (40 ml). After decanting, the solvents were evaporated and the residue containing the quaternary ammonium salt was dried overnight in air and subsequently dissolved with 2-amino-2-methyl-1-propanol (4 ml) and water (0.5 ml). The solution was heated up to 110°C which enabled the removal of one methyl group to occur within 1 hour. The demethylation was accompanied by partial decomposition to red impurities. The reaction mixture was then allowed to cool down to ambient temperature and water (20 ml) and ethyl acetate (60 ml) were added. The resulting two-phase mixture was transferred to a separatory funnel and upon addition of ethyl acetate (75 ml) the organic layer was washed with water (2 x 275 ml), and subsequently filtered off and evaporated to dryness. A red-brown waxy solid (0.89 g) was dissolved in dichloromethane (5 ml) purified by column and chromatography (1 inch diameter column, 50 ml silica gel suspended in hexane, eluent dichloromethane:ethyl acetate, 9:1). The orange fraction (100 ml) was collected and evaporated to dryness yielding a yellow solid (0.57 g, 32%). The moderate yield of the methylation is presumably due to competing polymerisation of 5-amino-1-indanone to a polyimine in the first stage of the reaction, analogously to the self-condensation of 4-aminobenzaldehyde.[7]

^{1}H NMR (500 MHz, 298K, CDCl$_3$+TMS): 7.63 (d, J$_{ortho}$ = 8.8 Hz, 1H), 6.69 (dd, J$_{ortho}$ = 8.8 Hz, J$_{meta}$ = 2.2 Hz, 1H), 6.60 (apparent broad singlet, 1H), 3.08 (s, 6H), 3.03 (t, J = 6.3 Hz, 2H), 2.63 (m, J = 6.0 Hz, 2H).

^{13}C NMR (125 MHz, 298K, CDCl$_3$+TMS): 204.73 (C=O), 157.94, 154.93, 125.81, 125.17, 111.75, 106.97, 40.37 (NMe$_2$), 36.41, 25.89.

Melting point: 114-116°C (lit.: 115-116°C[8]).

Synthesis of MGLA-C5 (5'-(dimethylamino)-3H-spiro[2-benzofuran-1,1'-indan]-3-one)
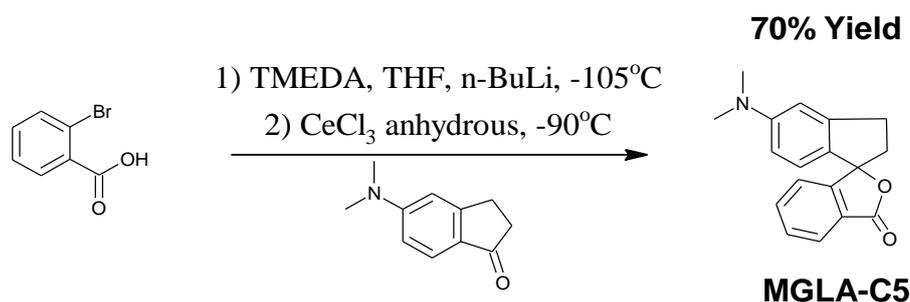
The reaction was carried out under an argon atmosphere. To 2-bromobenzoic acid (0.51 g, 2.5 mmol) charged in a three-necked round bottom flask (100 ml) was added tetramethylethylenediamine (TMEDA) (1 ml, 6.7 mmol) through a septum. After 30 minutes, anhydrous THF (20 ml) was also added through the septum. With stirring, the mixture was additionally deoxygenated by argon bubbling for 15 minutes. The almost colourless solution was cooled down to -105°C with a 1-propanol/liquid nitrogen bath, and n-butyllithium in hexane (1 ml, 2.5 mmol) was slowly added with a syringe for 5 minutes, so that temperature in the flask did not exceed -100°C. After the reaction mixture solidified, it was warmed up to -80°C, then again cooled down to -95°C, and the remaining portion of n-butyllithium in hexane (1.5 ml, 3.75 mmol) was added slowly, so that temperature in the flask did not exceed -90°C. The reaction mixture (turbid yellow solution) was kept afterwards at -90°C for 30 minutes, whereupon solid anhydrous CeCl$_3$ (0.82 g, 3.33 mmol) was added and the resulting mixture was stirred for 30 minutes at -80°C. Subsequently, 5-(dimethylamino)-1-indanone (0.225 g, 1.3 mmol) was added to the reaction mixture and the mixture was warmed up to -30°C, whereupon the bath was removed. After several minutes, when the temperature of the mixture exceeded 0°C, water (60 ml), acetic acid (2 ml) and ethyl acetate (20 ml) were added. After 15 minutes, the mixture was transferred to a separatory funnel using additional ethyl acetate (150 ml), the aqueous layer was separated, and the organic layer was washed twice

with water (150 ml) and evaporated to dryness. The above procedure resulted in a brown oil (0.36 g) that was purified by column chromatography (1 inch diameter column, 50 ml silica gel suspended in hexane, eluent dichloromethane + 1% ethyl acetate), and subsequently repeatedly crystallised from a tetrahydrofuran/2-propanol mixture to give colourless transparent plates (257 mg, yield 70%).

<u>^{1}H NMR</u> (500 MHz, 298K, CDCl$_3$+TMS): 7.94 (d, J$_{ortho}$=7.6 Hz, 1H); 7.66 (m, J$_{ortho}$=7.2 Hz, J$_{meta}$=0.6 Hz, 1H); 7.55 (m, J$_{ortho}$=7.3 Hz, 1H); 7.31 (d, J$_{ortho}$=7.5 Hz, 1H); 6.68 (m, J$_{meta}$=1.6 Hz, 1H); 6.62 (m, J$_{ortho}$=8.5 Hz, 1H); 6.53 (m, J$_{ortho}$=8.4 Hz, J$_{meta}$=2.2 Hz, 1H); 3.31-3.38 (m, J=7.9 Hz, 1H); 3.04-3.10 (m, J$_1$=6.1 Hz, J$_1$=16.1 Hz, 1H); 2.98 (s, 6H); 2.64-2.67 (m, J$_1$=7.9 Hz, J$_1$=5.3 Hz, 2H).

<u>^{13}C NMR</u> (125 MHz, 298K, CDCl$_3$+TMS): 169.93 (C=O); 152.46; 152.21; 146.90; 134.15; 129.00; 128.32; 126.80; 125.10; 124.55; 122.25; 111.66; 107.73; 96.60 (C sp^3); 40.61; 40.04; 30.67.

<u>HRMS (EI+)</u>: calculated for C$_{18}$H$_{17}$NO$_2$: (M$^+$): 279.1254; found:279.1267; error: 4.65 ppm.

<u>Elemental analysis</u>: calculated: C(77.40%), H(6.13%), N(5.01%), O(11.46%); found C(77.35%), H(6.41%), N(4.98%).

Melting point (THF/2-propanol): 153-154°C.

Dehydration of CeCl$_3$ heptahydrate

A 250 ml round-bottom flask equipped with a large magnetic stir bar was consecutively charged with CeCl$_3$·7H$_2$O (18.6 g, 50 mmol) and toluene (p.a. grade, 100 ml). The solvent receiver with inert gas inlet and outlet was attached to the flask and the content of the flask was subsequently distilled for 6 hours under an inert gas atmosphere under very vigorous stirring. The initially colourless solution, after half volume of the liquid had been distilled out, started to get turbid and a grey deposit appeared, which started to stick to the bottom of the flask. When approximately 10 ml of the liquid remained in the flask, the flask was cooled down, all remaining liquid was decanted, and the light beige crust was dried under a diaphragm pump. Subsequently, the obtained product (14.67 g) was removed from the flask with a metal spatula. [Caution! The solid adheres firmly to the surface of the flask and a misuse of the spatula may result in flask perforation.] The retrieved gray solid was ground and put in a three-necked round bottom flask (100 ml) with a large magnetic stir bar and heated for several hours under argon stream, while gradually increasing temperature up to 180°C and

maintaining the stir bar in a slow motion, until the mass of the flask with its contents was not changing further. A light beige powder was collected (12.13 g). The cerium salt so obtained can be stored under an inert gas atmosphere or in a desiccator for at least one year. It is essential that, before each reaction, a weighted amount of the cerium salt is additionally dried for 1 hour in an inert gas stream at 180°C.

NMR data
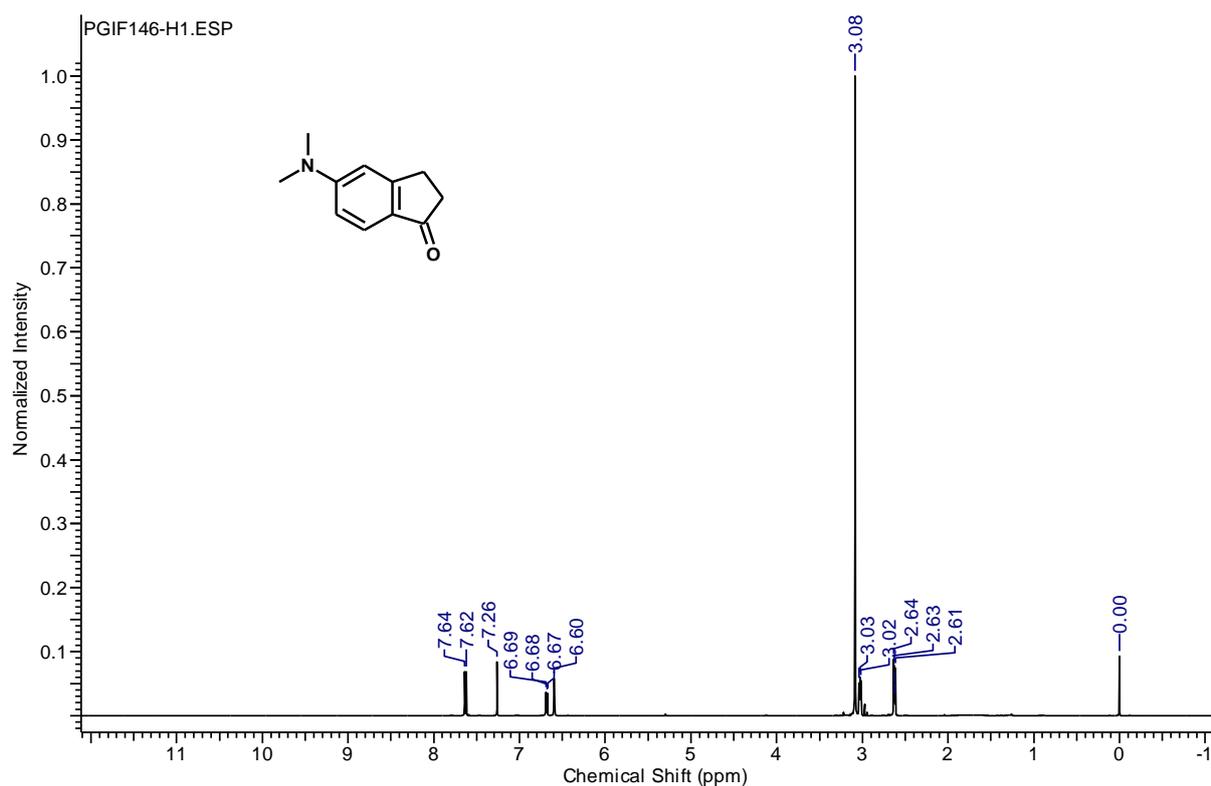
Figure S1. ^{1}H NMR spectrum of 5-DMAI.
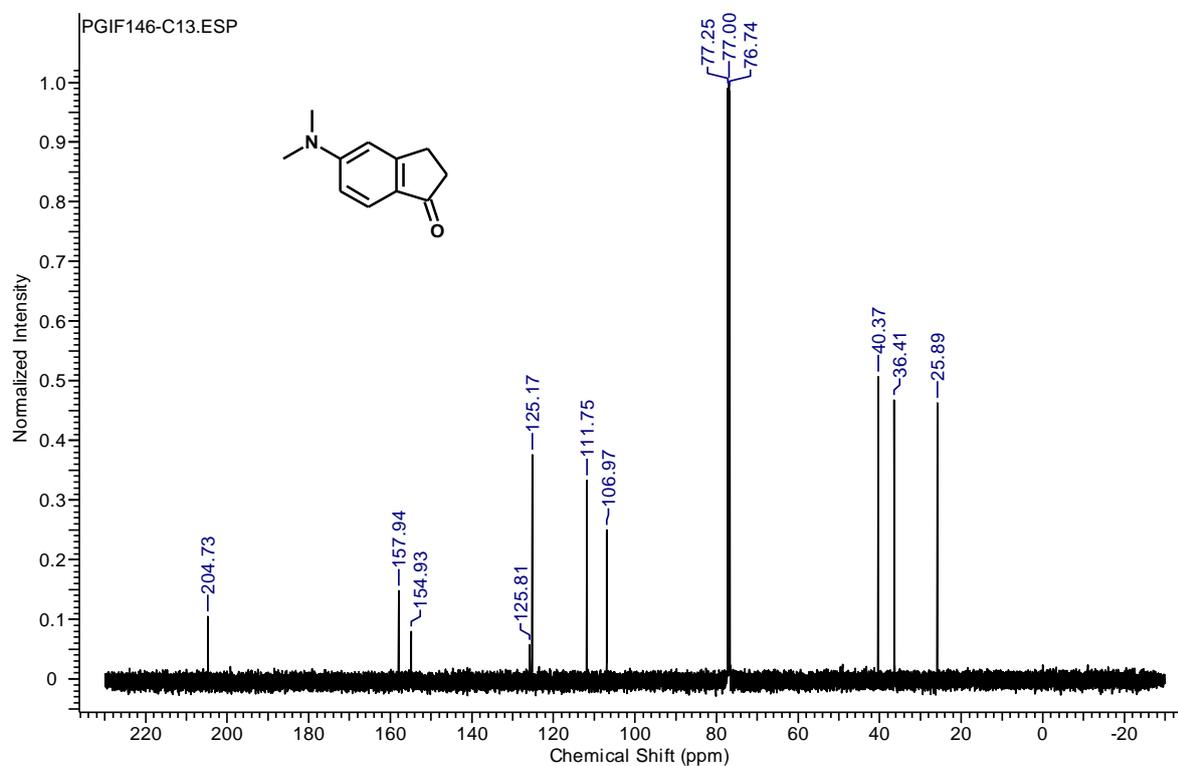
Figure S2. ^{13}C NMR spectrum of 5-DMAI.
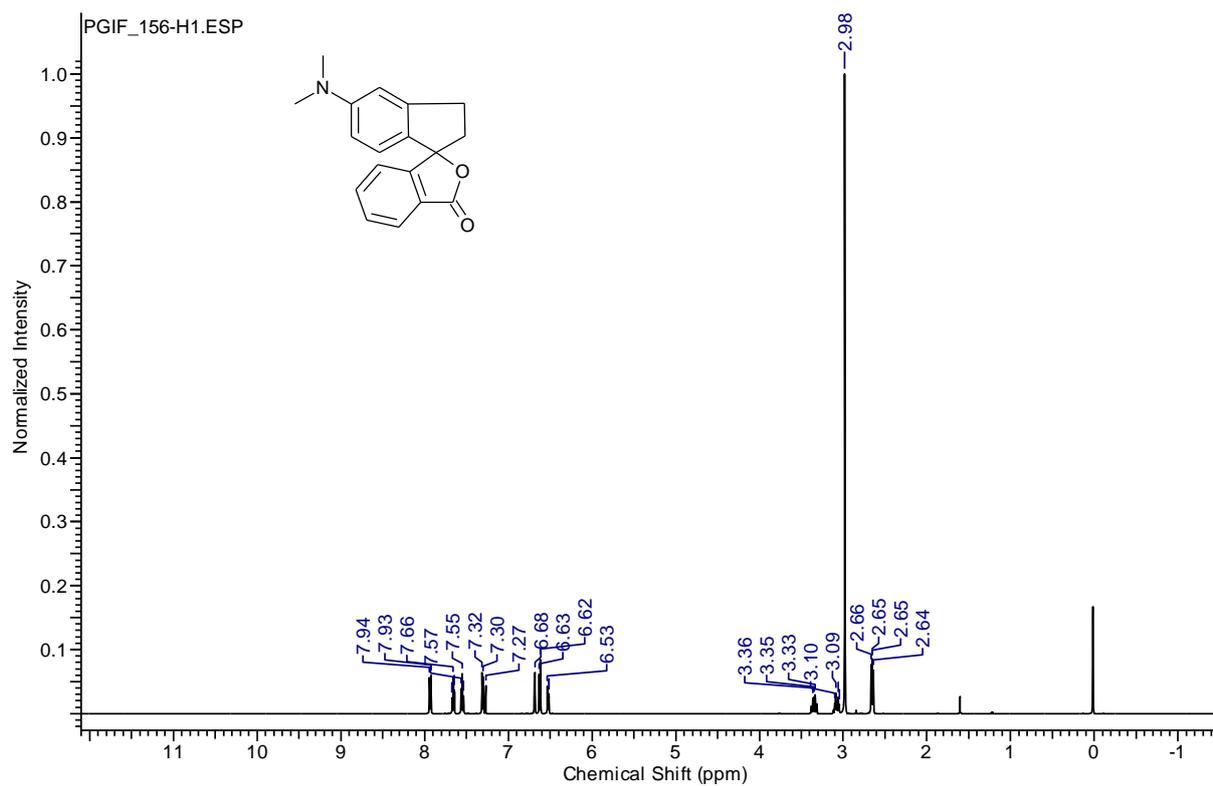
Figure S3. ^{1}H NMR spectrum of MGLA-C5.
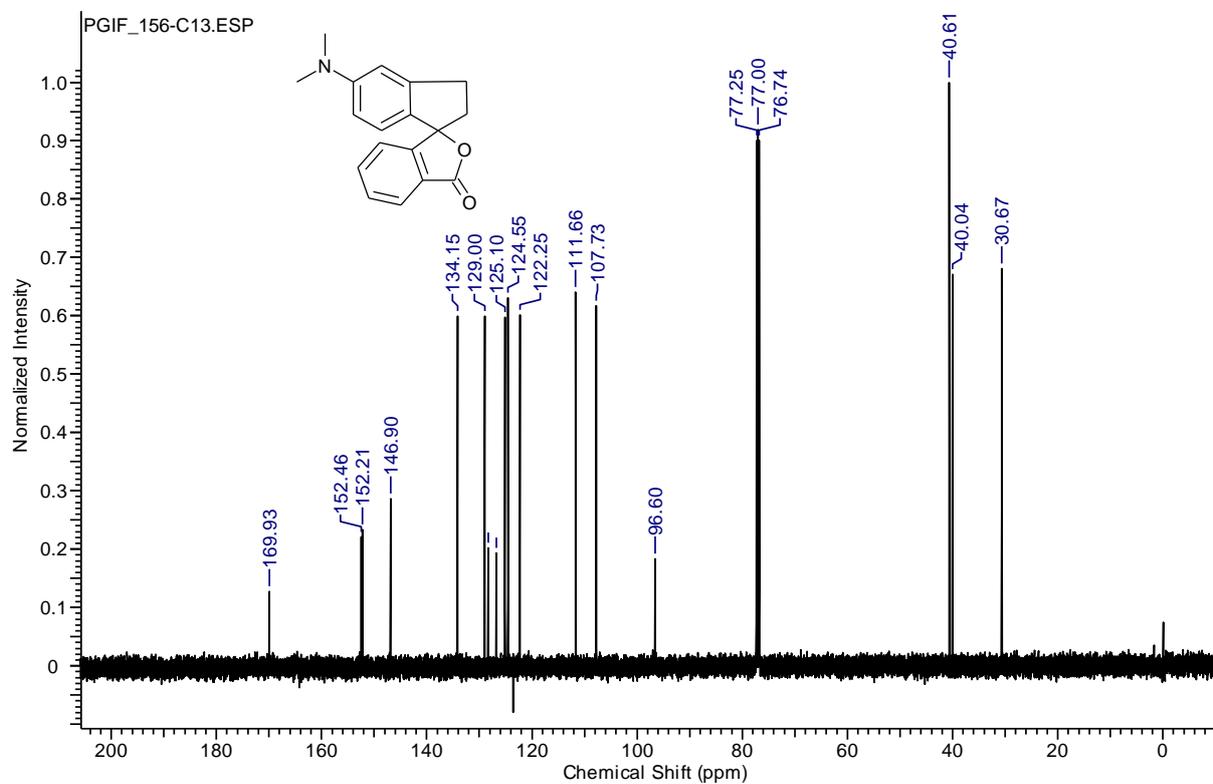
Figure S4. ^{13}C NMR spectrum of MGLA-C5.

Mass Spectrometry data
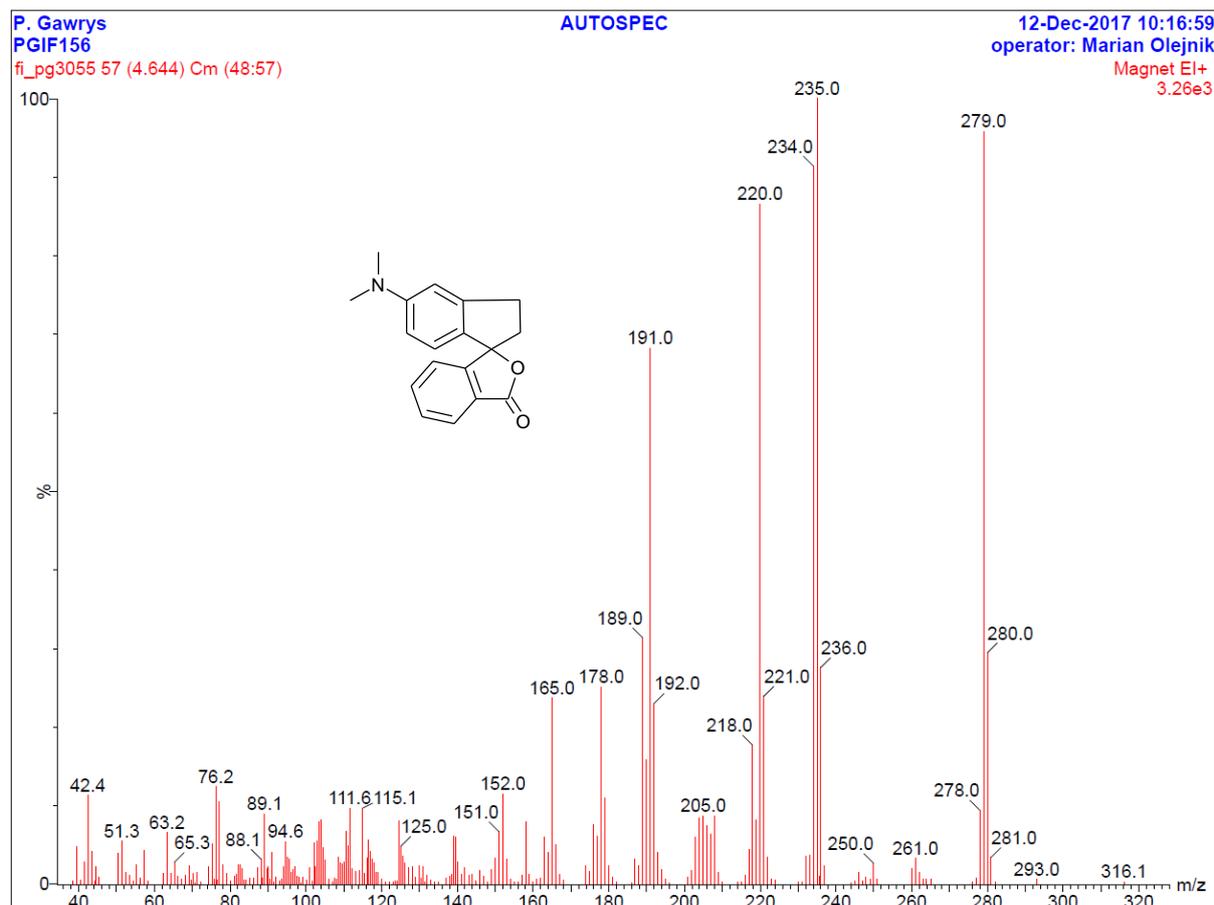
Figure S5. Low resolution (EILR) mass spectrum of MGLA-C5

Figure S6. High resolution (EIHR) mass spectrum of MGLA-C5.

X-ray crystallography data

Crystal data for **MGLA-C5**: $C_{18}H_{17}NO_2$, $M = 279.32$, colourless block, $0.272 \times 0.256 \times 0.146$ mm, monoclinic, space group $P2_1$, $a = 7.8987(7)$, $b = 6.2421(6)$, $c = 14.872(1)$ Å, $\beta = 103.530(5)°$, $V = 712.9(1)$ Å^3, $Z = 2$, $D_c = 1.301$ g/cm^3, $F_{000} = 296$, measurement device Bruker D8 VENTURE DUO, Cu$K\alpha$ radiation, $\lambda = 1.54178$ Å, $T = 150(2)$K, $2\theta_{max} = 129.9°$, 4004 reflections collected, 2029 unique ($R_{int} = 0.040$). The structure was solved and refined using the programs XT, VERSION 2014/4 and SHELXL-2014/7, respectively.[9] Final $GooF = 1.08$, $R = 0.034$, $wR = 0.082$, R indices based on 1916 reflections with $I > 2(\sigma I)$ (refinement on F^2), 193 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 0.676$ mm^{-1}. Absolute structure parameter = 0.2(2).[10]

The crystal data is deposited in The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/structures), CCDC number: 1909630.

Table S1. Bond lengths (Å) for **MGLA-C5**

O2-C2	1.207(3)	O1-C2	1.363(3)
O1-C1	1.488(3)	N1-C18	1.442(4)
N1-C17	1.444(4)	N1-C13	1.379(4)
C9-C10	1.543(4)	C3-C8	1.377(4)
C7-C8	1.390(4)	C2-C3	1.473(3)
C6-C7	1.385(4)	C1-C8	1.501(4)
C5-C6	1.398(4)	C13-C14	1.414(4)
C4-C5	1.383(4)	C12-C13	1.408(4)
C3-C4	1.391(4)	C11-C12	1.382(4)
C1-C9	1.527(4)	C11-C16	1.396(4)
C1-C16	1.505(4)	C10-C11	1.514(4)
C14-C15	1.381(4)	C15-C16	1.393(4)

Table S2. Selected bond angles (°) for **MGLA-C5**

O1-C2-C3	107.9(2)	O2-C2-C3	130.6(3)
O1-C1-C8	102.2(2)	O1-C1-C9	107.4(2)
C8-C3-C2	108.4(2)	O1-C1-C16	108.9(2)
C8-C1-C16	118.3(2)	C8-C3-C4	122.5(2)
C4-C3-C2	129.1(2)	C8-C1-C9	116.8(2)
C3-C8-C1	110.0(2)	C7-C8-C1	130.0(3)
C2-O1-C1	111.28(19)	C7-C6-C5	121.6(2)
C18-N1-C17	118.1(2)	C6-C7-C8	118.0(3)
C12-C13-C14	118.1(3)	C5-C4-C3	117.5(3)
C12-C11-C10	129.0(3)	C1-C9-C10	104.8(2)
C11-C10-C9	102.6(2)	C16-C1-C9	102.8(2)
C15-C16-C1	130.3(2)	C16-C11-C10	109.8(2)
C11-C16-C1	110.2(2)		

Table S3. Selected torsion angles (°) for **MGLA-C5**

C2-O1-C1-C8	-4.9(3)	C2-O1-C1-C16	-130.8(2)
C2-O1-C1-C9	118.5(2)	C1-O1-C2-O2	-175.6(2)
C1-O1-C2-C3	4.9(3)	O2-C2-C3-C8	177.7(3)
O1-C2-C3-C8	-2.9(3)	O2-C2-C3-C4	-3.2(5)
O1-C2-C3-C4	176.3(3)	C16-C1-C8-C3	122.6(3)
O1-C1-C8-C3	3.0(3)	O1-C1-C8-C7	-176.7(3)
C9-C1-C8-C3	-113.9(3)	C9-C1-C8-C7	66.4(4)
C16-C1-C8-C7	-57.1(4)	C8-C1-C9-C10	-161.6(2)
O1-C1-C9-C10	84.4(3)	C1-C9-C10-C11	29.1(3)
C16-C1-C9-C10	-30.4(3)	C9-C10-C11-C16	-16.9(3)
C9-C10-C11-C12	162.5(3)	C17-N1-C13-C12	10.0(4)
C18-N1-C13-C12	175.0(3)	C17-N1-C13-C14	-170.9(3)
C18-N1-C13-C14	-5.8(4)	O1-C1-C16-C15	86.7(3)
C10-C11-C16-C1	-2.3(3)	C9-C1-C16-C15	-159.6(3)
C8-C1-C16-C15	-29.3(4)	C8-C1-C16-C11	151.0(2)
O1-C1-C16-C11	-93.0(3)	C9-C1-C16-C11	20.8(3)

Table S4. Hydrogen bond distances (Å) and angles (°) for **MGLA-C5**

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C9-H9A...O2	0.99	2.64	3.408(4)	134.9

S3 Primary charge separation rate in MGLA-C5

At room temperature, a number of leuco derivatives of malachite green (MG) including leucomalachite green (MGH), MG leucocarbinol (MGOH) or MG leuconitrile (MGCN) (Figure S7) have low energy absorption spectra similar to those of N,N-dimethylaniline (DMA),[11] and their fluorescence comes from the vibrationally- and solvent-equilibrated locally excited (LE) state centred on DMA. The absence of fluorescence from the LE state in MGLA-C5 (similarly as in malachite green lactone (MGL)[12] and its single-donor analogue MGLA[13]) indicates that the ^{1}LE state is efficiently deactivated via transition to the fluorescent ^{1}CT state. In more polar solvents where the MGLA-C5 fluorescence band is considerably red-shifted (e.g. in BA or ACN, Figure 2), the deactivation is manifested by a close-to-zero fluorescence signal in the spectral region corresponding to the emission of the isolated DMA chromophore.
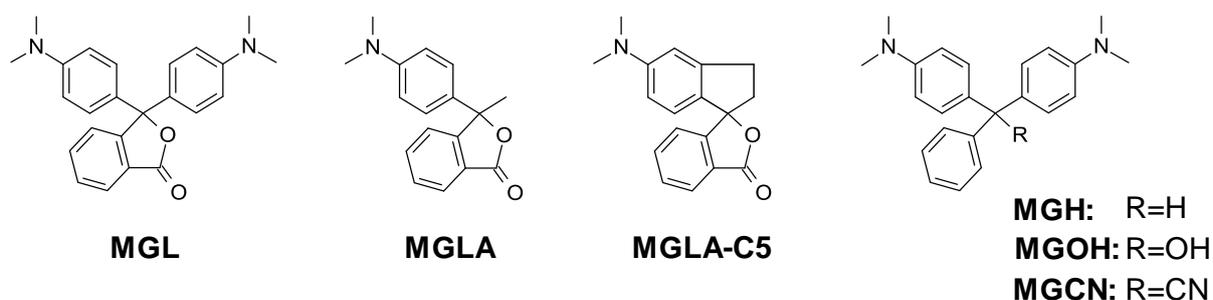
Figure S7. Structural formulae of MGL, MGLA, MGLA-C5 and MG leuco derivatives.

With an approach similar to that applied for MGL[12] one can obtain the lower limit for the rate constant of the intramolecular deactivation of the ^{1}LE state of DMA chromophore in MGLA-C5, and identifying the deactivation with the electron transfer process − estimate the approximate time constant for the primary electron transfer, k_{ET}. The upper limit for the integrated room temperature fluorescence intensity in the spectral region where possible fluorescence from insulated DMA chromophore in ACN would occur (31250-25000 cm^{-1}), can be estimated as $7.6 \cdot 10^{-3}$ times lower than that of the fluorescence band extending from 24000 to below 12500 cm^{-1} (Figure 2). The factor is comparable to that found for MGLA in ACN ($6.9 \cdot 10^{-3}$),[13] and considering the fluorescence quantum yield for MGLA-C5 in ACN ($\Phi_{MGLA-C5}$=0.001, Table 1) the quantum yield of a possible fluorescence from the DMA-centred ^{1}LE state in MGLA-C5, Φ_{LE}, is lower than $7.6 \cdot 10^{-6}$. Comparing with Φ_{DMA}=0.11 for DMA in ACN,[14] one obtains a reduction in fluorescence quantum yield from the ^{1}LE state in MGLA-C5 by a factor greater than $1.45 \cdot 10^4$, which − as in MGL and MGLA − implies a very

effective ultrafast deactivation of the primarily excited ^{1}LE state to the emitting ^{1}CT state. Assuming a first-order kinetics for the deactivation and neglecting vibrational relaxation upon excitation, k_{ET} can be roughly estimated by comparing Φ_{DMA} in ACN with the upper limit of Φ_{LE} estimated above: $k_{ET} = (\Phi_{DMA}/\Phi_{LE})(1/\tau_{DMA})$, where $\tau_{DMA} = 3.8$ ns is the fluorescence lifetime of DMA in ACN.[14] The rate constant of the electronic relaxation process in MGLA estimated with this formula, $k_{ET} \geq 3.8 \cdot 10^{12} \approx 4 \cdot 10^{12}$ s^{-1}, indicates that the primary electronic relaxation in MGLA is completed on a sub-250 fs time scale.

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