Direct coupling of carbenium ions with indoles and anilines for the synthesis of cationic $\pi$-conjugated dyes

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1. General remarks

CH$_2$Cl$_2$ and Et$_2$O employed for purification were technical grade. Acetonitrile and $N$-methyl-2-pyrrolidinone (NMP) were analytical grade. Bis(para-methoxyphenyl)phenylmethyl chloride (PMP:PhCCl$_2$) was purchased from Aldrich® and used without any further purification. tris-(2,6-Dimethoxyphenyl)carbenium tetrafluoroborate 1 was prepared on gram scale using previously reported conditions. 5-(tert-Butylcarbamate)indole, 1-methylindole and 1,2-dimethylindole were prepared according to described procedures respectively from 5-aminindoled$_2$, indole$^3$ and 2-methylindole.$^4$

NMR spectra were recorded on Brucker AMX-500 or AMX-400 or ARX-300 at room temperature. For $^1$H NMR, Chemical shifts are given in ppm relative to Me$_4$Si with solvent resonances used as internal standards (7.26 ppm for CDCl$_3$, 5.32 ppm for CD$_2$Cl$_2$, 2.50 ppm for DMSO-$d_6$ and 1.94 for CD$_3$CN). Following abbreviations were employed for multiplicity: s = singulet, br = broad singulet, d = doublet, t = triplet, q = quintuplet, dd = doublet of doublet; dt = doublet of triplet, m = multiplet; $J$ = coupling constant (Hz). For $^{13}$C NMR, chemicals shifts were given in ppm relative to Me$_4$Si with solvent resonances used as internal standards (77.1 ppm for CDCl$_3$, 53.8 ppm for CD$_2$Cl$_2$, 39.5 for DMSO-$d_6$ and 118.2 for CD$_3$CN). IR spectra were recorded with a Perkin-Elmer 1650. FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points (M.P.) were measured in open capillary tubes with a Buchi Melting Point M-565 apparatus (5 °C/min grade) and are uncorrected. $R_f$ were measured on TLC Silica gel 60 F254 plates purchased from Merck. Electrospray mass spectra were obtained on a Finnigan SSQ 7000 spectrometer by the Department of Mass Spectroscopy of the University of Geneva. UV/Visible spectra were obtained using a Cary 50 spectrophotometer.

2. Synthesis and characterization of compounds 4, 6 and 7

General procedure for the oxidative cross-deshydrogenative coupling: To a solution of tris(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 1 in NMP were added PMP$_2$PhCCl and either an indole or an aniline. The mixture was then stirred for the indicated period, conversion of starting material being monitored by TLC and MS-ESI. Aqueous NaBF$_4$ (0.2 M) was then added and resulting suspension was filtered. Unless otherwise stated, the collected solid was purified by a dissolution in CH$_2$Cl$_2$ and a selective precipitation upon addition of Et$_2$O.

(4-(1H-Indol-3-yl)-2,6-dimethoxyphenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4a: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP$_2$PhCCl (0.55 mmol) and 64 mg of indole (0.55 mmol) were stirred for 5 h in 1.5 mL of NMP to yield, after purification, 242 mg of wanted compound 4a as a deep blue solid (77%).

R$_f$ = 0.48 (CH$_2$Cl$_2$/MeOH 90:10). $^1$H NMR (400 MHz, CD$_3$CN) δ (ppm): 11.55 (s, 1H), 8.52 (s, 1H), 8.27 – 7.95 (m, 1H), 7.82 – 7.59 (m, 1H), 7.43 – 7.38 (m, 2H), 7.35 (t, J = 8.7 Hz, 2H), 6.95 (s, 2H), 6.61 (d, J = 8.4 Hz, 4H), 3.68 (s, 6H), 3.52 (s, 12H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ (ppm): 167.07 (C), 164.71 (C), 159.70 (C), 158.55 (C), 139.22 (C), 139.16 (CH), 132.83 (CH), 127.32 (C), 125.16 (C), 125.02 (CH), 124.33 (CH), 123.48 (C), 122.26 (CH), 117.70 (C), 114.46 (CH), 105.12 (CH), 100.60 (CH), 57.50 (CH$_3$), 56.60 (CH$_3$). $^{19}$F NMR (282 MHz, CD$_3$CN) δ (ppm): -151.76, -151.81. UV/VIS (CH$_3$CN, 5.10$^{-4}$ M), $\lambda_{max}$ ($\varepsilon$): 576 (32530). MS (ESI$^+$), m/z (%): 538.3 (M$^+$, 44), 266.4 (100). M.P. = 245 °C (decomposition). IR (ATR) $\upsilon$ (cm$^{-1}$): 3269, 2175, 1605, 1585, 1531, 1470, 1417, 1363, 1287, 1238, 1193, 1167, 1102, 1063, 1004, 932, 874, 824, 790, 766, 732, 657, 621. HRMS (ESI$^+$) calc. for C$_{33}$H$_{32}$O$_6$N$^+$ [M$^+$]: 538.2224. Found: 538.2232.
Bis(2,6-dimethoxyphenyl)(4-(5-fluoro-1H-indol-3-yl)-2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4b: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP₂PhCCl (0.55 mmol) and 95 mg of 5-fluoroindole (0.70 mmol) were stirred for 26.5 h in 1.5 mL of NMP to yield, after purification, 231 mg of wanted compound 4b as a deep blue solid (72%).

Rf = 0.42 (CH₂Cl₂/MeOH 90:10). ¹H NMR (400 MHz, CD₂CN) δ (ppm): 10.69 (s, 1H), 8.46 (s, 1H), 7.79 (dd, J = 10.2, 2.4 Hz, 1H), 7.64 (dd, J = 9.0, 4.6 Hz, 1H), 7.37 (t, J = 8.4 Hz, 2H), 7.18 (td, J = 9.1, 2.4 Hz, 1H), 6.86 (s, 2H), 6.61 (d, J = 8.4 Hz, 4H), 3.69 (s, 6H), 3.52 (s, 12H). ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 166.79 (C), 165.52 (C), 160.57 (C), 159.07 (C), 158.20 (d, J = 10.2 Hz, C), 139.37 (CH), 135.25 (CH), 126.84 (C), 125.28 (d, J = 10.2 Hz, C), 123.06 (C), 116.97 (C), 115.16 (d, J = 10.1 Hz, CH), 112.39 (d, J = 25.9 Hz, CH), 107.44 (d, J = 25.4 Hz, CH), 104.69 (CH), 100.19 (CH), 57.14 (CH₃), 56.17 (CH₃). ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -120.50, -151.93, -151.99.

UV/VIS (CH₂CN, 5.10⁻⁵ M), λₓ-max (ε): 596 (30270).

MS (ESI⁺, m/z): 556.3 (M⁺+, 50), 284.4 (100).


(2,6-dimethoxy-4-(5-methyl-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)methylium tetrafluoroborate 4c: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP₂PhCCl (0.55 mmol) and 79 mg of 5-methylindole (0.60 mmol) were stirred for 2 h in 2 mL of NMP to yield, after purification, 269 mg of wanted compound 4c as a deep blue solid (84%).

Rf = 0.56 (CH₂Cl₂/MeOH 90:10). ¹H NMR (400 MHz, CD₂CN) δ (ppm): 10.76 (bs, 1H), 8.44 (s, 1H), 7.88 (s, 2H), 7.54 (d, J = 8.3 Hz, 1H), 7.34 (t, J = 8.4 Hz, 2H), 7.24 (d, J = 8.3 Hz, 1H), 6.92 (s, 2H), 6.61 (d, J = 8.4 Hz, 4H), 3.68 (s, 6H), 3.52 (s, 12H), 2.51 (s, 3H). ¹³C NMR (100 MHz, CD₂CN) δ (ppm): 168.02 (C), 166.90 (C), 161.01 (C), 159.68 (C), 137.79 (C), 137.15 (CH), 134.72 (C), 133.88 (CH), 128.38 (C), 127.10 (CH), 126.13 (C), 124.41 (C), 122.34 (CH), 118.22 (C), 114.49 (CH), 105.61 (CH), 101.52 (CH), 57.72 (CH₃), 56.86 (CH₃), 21.90 (CH₃). ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm): -151.61, -151.67.

UV/VIS (CH₂CN, 5.10⁻⁵ M), λₓ-max (ε): 606 (27970).

MS (ESI⁺, m/z): 552.5 (M⁺+, 36), 280.5 (100). M.P. = 231 °C (decomposition). IR (ATR) υ (cm⁻¹): 1608,
(2,6-Dimethoxy-4-(5-methoxy-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4d: following general procedure, 255 mg of starting material (0.5 mmol), 186 mg of PMP₂PhCCI (0.55 mmol) and 81 mg of 5-methoxyindole (0.55 mmol) were stirred for 1.5 h in 1.5 mL of NMP to yield after purification, 295 mg of wanted compound 4d as a deep blue solid (90 %).

δ (ppm): 10.80 (s, 1H), 8.42 (s, 1H), 7.55 (d, \(J = 8.9\) Hz, 1H), 7.51 (s, 1H), 7.34 (t, \(J = 8.4\) Hz, 1H), 7.02 (dd, \(J = 8.9, 2.3\) Hz, 1H), 6.89 (s, 2H), 6.60 (d, \(J = 8.4\) Hz, 4H), 3.88 (s, 3H), 3.67 (s, 6H), 3.52 (s, 12H).

(4-(5-((tert-butoxycarbonyl)amino)-1H-indol-3-yl)-2,6-dimethoxyphenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4e: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP₂PhCCI (0.55 mmol) and 139 mg of 5-((tert-butylicarbamate)indole (0.60 mmol) were stirred for 3 h in 1.5 mL of NMP, to yield, after purification, 255 mg of wanted compound 4e as a deep blue solid (69 %).

δ (ppm): 10.89 (s, 1H), 8.32 (s, 1H), 7.73 (s, 1H), 7.55 (d, \(J = 8.8\) Hz, 1H), 7.39 (dd, \(J = 8.8, 2.0\) Hz, 1H), 7.34 (t, \(J = 8.4\) Hz, 1H), 6.93 (s, 2H), 6.61 (d, \(J = 8.4\) Hz, 4H), 3.69 (s, 6H), 3.52 (s, 12H), 1.49 (s, 9H).
(CH), 114.95 (CH), 111.75 (CH), 105.62 (CH), 101.34 (CH), 80.66 (C), 57.72 (CH3), 56.87 (CH3), 28.54 (CH3). 19F NMR (282 MHz, CDCl3) δ (ppm): -151.82, -151.87. UV/VIS (CH3CN, 5.105 M), λmax (ε): 626 (47200). MS (ESI+, m/z): 653.5 (M+, 34), 697.5 (M+(CH3)2C, 100), 553.3 (M+(CH3)2C-CO2, 34), 325.3 (82). M.P. = 216 °C (decomposition). IR (ATR) ν (cm-1): 3317, 2931, 1714, 1610, 1588, 1529, 1473, 1409, 1366, 1338, 1290, 1233, 1159, 1101, 1060, 1005, 932, 889, 850, 793, 739, 716, 615. HRMS (ESI+) calc. for C38H41O8N2+ [M+]: 653.2857. Found: 653.2844.

(2,6-dimethoxy-4-(2-methyl-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4f: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP2PhCl (0.55 mmol) and 72 mg of 2-methylindole (0.55 mmol) were stirred for 4 h in 1.5 mL of NMP to yield, after purification, 226 mg of wanted compound 4f as a deep blue solid (70 %). 

Rf = 0.44 (CH2Cl2/MeOH 90:10). 1H NMR (400 MHz, CD2Cl2) δ (ppm): 10.77 (s, 1H), 8.00 – 7.74 (m, 1H), 7.69 – 7.49 (m, 1H), 7.49 – 7.09 (m, 4H), 6.72 (s, 2H), 6.55 (d, J = 8.4 Hz, 4H), 3.64 (s, 6H), 3.56 (s, 12H), 2.87 (s, 3H). 13C NMR (100 MHz, CD2Cl2) δ (ppm): 167.01 (C), 165.96 (C), 161.04 (C), 159.25 (C), 148.01 (C), 137.57 (C), 133.53 (CH), 127.66 (C), 126.91 (C), 124.79 (CH), 123.98 (C), 123.72 (CH), 120.67 (CH), 116.69 (C), 114.00 (CH), 105.06 (CH), 102.70 (CH), 57.08 (CH3), 56.77 (CH3), 16.48 (CH3). 19F NMR (282 MHz, CD3CN) δ (ppm): -149.02, -149.08. MS (ESI+, m/z): 552.3 (M+, 34), 280.5 (100), 220.1 (28). UV/VIS (CH3CN, 5.105 M) λmax (ε): 636 (29670). M.P. = 195 °C (decomposition). IR (ATR) ν (cm-1): 3297, 2937, 2838, 1606, 1586, 1470, 1386, 1341, 1286, 1236, 1168, 1104, 995, 930, 825, 788, 733, 601. HRMS (ESI+) calc. for C38H38O8N2+ [M+]: 552.2381. Found: 552.2374.

(2,6-Dimethoxy-4-(1-methyl-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4g: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP2PhCl (0.55 mmol) and 107 mg of 1-methylindole (107 mg, 0.83 mmol) were stirred for 5.5 h in 1.5 mL of NMP to yield, after purification, 247 mg of wanted compound 4g as a deep blue solid (77 %).

Rf = 0.52 (CH2Cl2/MeOH 90:10). 1H NMR (400 MHz, CD2Cl2) δ (ppm): 8.63 (s, 1H), 8.09 – 7.91 (m, 1H), 7.57 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 7.30 (t, J = 8.4
Hz, 2H), 6.93 (s, 2H), 6.54 (d, J = 8.4 Hz, 4H), 4.02 (s, 3H), 3.70 (s, 6H), 3.55 (s, 12H). $^{13}$C NMR (100 MHz, CD$_2$Cl) δ (ppm): 167.52 (C), 164.93 (C), 160.04 (C), 159.13 (C), 140.97 (CH), 140.25 (C), 133.12 (C), 128.11 (C), 126.38 (C), 125.13 (CH), 124.60 (CH), 123.97 (C), 121.88 (CH), 117.28 (C), 112.47 (CH), 105.03 (CH), 100.77 (CH), 57.33 (CH$_3$), 56.76 (CH$_3$), 34.75 (CH$_3$).

$^{19}$F NMR (282 MHz, CD$_2$CN) δ (ppm): -151.80, -151.85.

MS (ESI$^+$, m/z): 552.3 (M$^+$, 44), 280.5 (100).

UV/VIS (CH$_3$CN, 5.10$^{-5}$ M), $\lambda_{\text{max}}$ (ε): 630 (56270). M.P. = 217 °C (decomposition).

IR (ATR) υ (cm$^{-1}$): 2941, 2835, 1615, 1587, 1541, 1519, 1773, 1447, 1437, 1409, 1381, 1357, 1287, 1254, 1227, 1186, 1140, 1114, 1089, 1060, 1021, 933, 881, 832, 781, 766, 732, 618.

HRMS (ESI$^+$) calc. for C$_{34}$H$_{34}$O$_6$N$^+$ [M$^+$]: 552.2381. Found: 552.2391.

Bis(2,6-dimethoxyphenyl)(4-(1,2-dimethyl-1H-indol-3-yl)-2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4h: following procedure 1, 255 mg of starting material (0.50 mmol), 186 mg of PMP$_2$PhCCl (0.55 mmol) and 80 mg of 1,2-dimethylindole (0.55 mmol) were stirred for 6 h in 1.5 mL of NMP to yield, after purification, 243 mg of wanted 4h compound as a deep blue solid (74%).

R$_f$ = 0.60 (CH$_2$Cl$_2$/MeOH 90:10). $^1$H NMR (400 MHz, CD$_3$CN) δ (ppm): 7.97 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.43 – 7.23 (m, 4H), 6.73 (s, 2H), 6.61 (d, J = 8.4 Hz, 4H), 3.83 (s, 3H), 3.64 (s, 6H), 3.54 (s, 12H), 2.79 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$CN) δ (ppm): 168.25 (C), 167.50 (C), 161.02 (C), 159.85 (C), 147.96 (CH), 139.39 (C), 134.37 (C), 128.05 (CH), 126.66 (C), 124.74 (CH), 124.46 (CH), 124.14 (C), 121.38 (CH), 116.60 (C), 112.07 (CH), 105.60 (CH), 104.02 (CH), 57.56 (CH$_3$), 56.83 (CH$_3$), 31.45 (CH$_3$), 14.23 (CH$_3$).

UV/VIS (CD$_3$CN, 5.10$^{-5}$ M), $\lambda_{\text{max}}$ (ε): 656 (42260). MS (ESI$^+$, m/z): 566.3 (M$^+$, 31), 294.5 (100). M.P. = 208 °C (decomposition).

HRMS (ESI$^+$) calc. for C$_{34}$H$_{36}$O$^+$ [M$^+$]: 566.2530. Found: 566.2552.

4-amino-4’-(bis(2,6-dimethoxyphenyl)methyl)-3’,5’-dimethoxy-[1,1’-biphenyl]-2-ol tetrfluoroborate 6: following modified procedure 1, 255 mg of starting material (0.50 mmol) and 65 mg of 3-aminophenol (0.60 mmol) were stirred for 6 h in 1.5 mL of NMP (no additive was added) to yield, after purification, 120 mg of wanted compound 6 as a deep green solid (39%).
Rf = 0.32 (CH2Cl2/MeOH 90:10). 1H NMR (400 MHz, CD3CN) δ (ppm): 7.69 (d, J = 9.0 Hz, 1H), 7.33 (t, J = 8.4 Hz, 2H), 7.03 (s, 2H), 6.59 (d, J = 8.4 Hz, 4H), 6.39 (dd, J = 9.0, 2.2 Hz, 1H), 6.28 (d, J = 2.1 Hz, 1H), 5.51 (bs, 2H), 3.55 (s, 6H), 3.50 (s, 12H). 13C NMR (100 MHz, CD3CN) δ (ppm): 167.09 (C), 166.60 (C), 163.19 (C), 162.63 (C), 159.69 (C), 157.62 (C), 134.69 (CH), 133.85 (CH), 128.28 (C), 124.52 (C), 115.15 (C), 110.24 (CH), 105.61 (CH), 103.61 (CH), 101.38 (CH), 57.32 (CH3), 56.84 (CH3).

19F NMR (282 MHz, CD3CN) δ (ppm): -151.75, -151.80. UV/VIS (CH3CN, 5.10×10-5 M), λmax (ε): 655 (44600). MS (ESI+) m/z (%): 530.3 (M+, 21), 258.4 (100), 505.5 (33). M.P. = 258.1 °C.

IR (ATR) υ (cm⁻¹): 3352, 1642, 1580, 1471, 1420, 1402, 1340, 1278, 1236, 1218, 1184, 1109, 1027, 933, 854, 808, 779, 731, 672, 578, 555. HRMS (ESI+) calc. for C31H32O7N+: 530.2173. Found: 530.2161.

(4‘-Amino-2’,3,5,5’-tetramethoxy-[1,1’-biphenyl]-4-yl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 7: following modified procedure I, 357 mg of starting material (0.70 mmol) and 129 mg of 2,5-dimethoxyaniline (0.84 mmol) were stirred for 14 h in 2.5 mL of NMP (no additive was added) to yield, after purification, 212 mg of wanted compound 7 as a deep green solid (46%).

Rf = 0.46 (CH2Cl2/MeOH 90:10). 1H NMR (400 MHz, CD3CN) δ (ppm): 7.32 (t, J = 8.4 Hz, 2H), 7.15 (s, 1H), 6.96 (s, 2H), 6.59 (d, J = 8.4 Hz, 4H), 6.49 (s, 1H), 5.72 (bs, 2H), 3.92 (s, 3H), 3.90 (s, 3H), 3.57 (s, 6H), 3.51 (s, 12H). 13C NMR (100 MHz, CD3CN) δ (ppm): 166.71 (C), 165.18 (C), 162.20 (C), 160.58 (C), 159.65 (C), 149.14 (C), 142.74 (C), 133.62 (CH), 128.37 (C), 124.56 (C), 115.72 (C), 112.72 (CH), 105.60 (CH), 104.14 (CH), 98.05 (CH), 57.31 (CH3), 57.04 (CH3), 57.02 (CH3), 56.84 (CH3). 19F NMR (282 MHz, CD2Cl2) δ (ppm): -152.71, -152.76. UV/VIS (CH3CN, 5.10×10-5 M), λmax (ε): 474 (9940), 700 (37090). MS (ESI+, m/z): 574.3 (M+, 42), 302.1 (100). M.P. = 240 °C (decomposition). IR (ATR) υ (cm⁻¹): 3342, 2922, 2840, 1647, 1610, 1587, 1545, 1471, 1147, 1428, 1402, 1374, 1353, 1333, 1244, 1231, 1202, 1108, 1063, 1019, 935, 843, 775, 748, 725, 711. HRMS (ESI+) calc. for C33H36O8N+: 574.2435. Found: 574.2440.
3. NMR evidence for the presence of compound 5 in crude mixtures

![NMR Spectra in CD$_2$Cl$_2$ of a) reduced product 5 formed according to a previously reported procedure; b) crude mixture of the reaction of 1 with 5-methoxyindole (2d); c) Salt [4d][BF$_4$].](image)

Note that the broad signal around 4.77 ppm in spectrum b) is attributed to the acid present in crude mixture.

4. NMR ($^1$H, $^{13}$C and $^{19}$F) and absorption (UV-Vis) spectra
Wavelength (nm)

\[ \varepsilon / \text{mol}^{-1} \text{L.cm}^{-1} \]


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    % Add your graph elements here

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5. Absorption properties

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**Table S1**: Absorption maximum wavelengths and extinction coefficient of hexamethoxycarbenium derivatives. All absorption spectra have been recorded in acetonitrile.

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**Table S2**: Absorption maxima of 1, 4a and 4f in various solvents.
Figure S2. Electronic absorption spectra of 1, 4a and 4f in various solvents.
6. Photophysics

Experimental details

Solvent. Acetonitrile (ACN, Fisher scientific, UK, > 99.9) and glycerol (Alfa Aesar, ultrapure, HPLC grade, stored under Ar) were used as received.

Steady-state spectroscopy. Electronic absorption spectra were obtained using a Cary 50 spectrophotometer. All the molar extinction coefficients were measured using $5 \times 10^{-6}$ to $5 \times 10^{-5}$ M solutions in acetonitrile. They are summarised with maximum absorption wavelengths in Table S1.

Fluorescence spectra were measured with a Jobin-Yvon (Horiba) Fluoromax 4, using 3 and 6 nm excitation and emission slits, respectively, 0.5 s accumulation time and taking the average of 10 spectra. The measurements were done with 1 to $5 \times 10^{-5}$ M solutions. The fluorescence quantum yield of 4a in glycerol has been measured upon 550 nm excitation with oxazine1 in ethanol ($\Phi_f = 0.11$) as reference.

Fluorescence up-conversion. The fluorescence up-conversion set-up has been described in detail elsewhere.2,3 Excitation was carried out at 450 nm using the frequency-doubled output of a Kerr-lens mode-locked Ti:Sapphire oscillator (Mai Tai HP, Spectra Physics). The polarization of pump pulses was at magic angle relative to that of the gate pulses at 900 nm. The pump intensity on the sample was 5µJ cm$^{-2}$ and the full width at half maximum of the instrument response function was ca. 230 fs. All measurements were performed in a 0.4 mm rotating cell and the absorbance of the samples at 450 nm was between 0.2 and 0.5. No photodegradation of the samples was observed throughout the measurements.

Transient electronic absorption. The femtosecond transient electronic absorption set-up has been described in detail previously.4,5 Excitation was performed at 400 nm using the frequency-doubled output of a standard 1-kHz Ti:Sapphire amplifier. The pump intensity on the sample was about 1 mJ/cm$^2$. All data were corrected for the chirp of the white light. The polarization of the pump pulse was at the magic angle relative to that of the probe pulse. The samples were located in a 1 mm quartz cell and stirred by nitrogen bubbling to avoid photodegradation. Their absorbance at 400 nm was 0.04. No noticeable photodegradation was observed throughout the measurements.

Quantum chemistry calculations. Ground-state gas-phase geometry optimization was performed at the density functional level of theory (DFT) using the CAM-B3LYP functionals,6 and the 6-31G* basis set. The electronic transitions were computed with time-dependent DFT (TD-DFT) using the same functional and basis set. The calculations were carried out using Gaussian 09.7
**Data**

*Quantum chemistry calculations*

![Figure S3](image.png)

**Figure S3.** Frontier molecular orbitals of 1 calculated at the CAM-B3LYP/6-31G* level of theory. The energy of three HOMOs is within 6 meV.

**Transient electronic absorption**

Figure S4a-c depicts transient absorption (TA) spectra recorded at several time delays after 400 nm excitation of 4a in ACN. The scaled steady-state absorption spectrum of 4a in ACN is also shown for comparison. These spectra are dominated by a negative band coinciding with the steady-state absorption spectrum that can be ascribed to the bleach of the absorption due to the depletion of the ground-state population. Additionally, two positive bands can be observed, one around 430 nm and the other at about 700 nm. The time evolutions of these two band differ considerably. Whereas the 430 nm band decays almost completely within 5 ps, the 700 nm band rises during the first 3-4 ps and decays on a 10-15 ps timescale. On the other hand, the negative band exhibits a biphasic decay, and has totally vanished after about 20 ps, pointing to a full recovery of the ground-state population. The time evolution and spectral position of the 700 nm band, i.e. on the red side of the ground-state bleach, are typical of an unrelaxed/vibrationally hot ground state. The temporal evolution of the TA spectra can be rationalized in terms of an A→B→C kinetic scheme, where A is the excited state of 4a, characterised by the 430 nm TA band, B is the unrelaxed ground state populated upon internal conversion from A, and C is the thermally equilibrated ground state. Global target analysis of the TA data assuming this scheme resulted to time constants of 1 ps and 7.4 ps for the internal conversion (A→B) and the relaxation to the
equilibrated ground state (B→C), respectively, and to the species associated difference absorption spectra depicted in Figure S4d.

**Figure S4.** (a-c) Transient absorption spectra recorded at various time delays after 400 nm excitation of 4a in acetonitrile; (d) species-associated difference absorption spectra resulting from a target global analysis assuming a A→B→C scheme. The dashed-dot line is the scaled steady-state absorption spectrum.

*Time-resolved fluorescence*

Time profiles of the fluorescence intensity measured at 720 nm with 4a in ACN upon 450 nm excitation are shown in Figure S5. This profile could be analysed using the convolution of the instrument response function and the sum of two exponential functions with 0.2 and 1.05 ps time constants. The relative amplitude of the slow component was found to increase with the detection wavelength. From the comparison with the transient absorption measurements, the 1.05 ps component can be ascribed to the decay of the excited-state population, whereas the 0.2 ps can be assigned to relaxation processes (vibrational and solvent relaxation) from the initially populated Franck-Condon excited state.
**Figure S5.** Fluorescence time profile measured with 4a in acetonitrile upon 450 nm excitation.

A qualitatively similar result was obtained with 4g in ACN with 0.17 ps and 0.95 ps time constants, the latter being assigned to the excited-state lifetime (Figure S6)

**Figure S6.** Fluorescence time profiles measured with 4g in acetonitrile upon 450 nm excitation.
