Supporting information

Controlling the Canonical/Zwitterionic Balance through Intramolecular Proton Transfer: a Strategy for Vapochromism

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S-I. GENERAL REMARKS AND ANALYSIS CONDITIONS

Reagents. All reagents were purchased from Alfa-Aesar and used as received. Column chromatography were performed using Silica 60M (0.04-0.063 mm) purchased from Macherey-Nagel. Optical properties were recorded in spectrophotochemical grade solvents. Compounds **7**¹ and **9**² were prepared following previously reported protocols. The synthesis of compound **3a** has been updated here since its previous publication.¹

Analytical methods and apparatus. NMR spectra were recorded on a JEOL ECS400 NMR spectrometer at room temperature. NMR chemical shifts are given in ppm (δ) relative to Me₄Si with solvent resonances used as internal standards (CDCl₃: 7.26 ppm for ¹H and 77.2 for ¹³C; Acetone-*d*₆: 2.05 ppm for ¹H and 29.8 for ¹³C; DMSO-d₆: 2.50 ppm for ¹H and 39.5 for ¹³C). UV-Vis-NIR absorption spectra were recorded on a VARIAN CARY 50 SCAN spectrophotometer at room temperature. IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer using a diamond ATR sampling. HRMS (ESI) and MS (ESI) analyses were performed on a QStar Elite (Applied Biosystems SCIEX) or a SYNAPT G2 HDMS (Waters) spectrometers by the "*Spectropole*" of the Aix-Marseille University. These two instruments were equipped with an ESI or MALDI source spectrometer.

Single Crystal X-ray Diffraction. Suitable crystals for compounds **3a** and **4** were obtained from slow evaporation from MeOH and CH₃CN, respectively. They were mounted on a Rigaku Oxford Diffraction SuperNova diffractometer and measured at 293K at the Cu radiation (λ =1.54184 Å). Data collection, reduction and multiscan ABSPACK correction were performed with CrysAlisPro (Rigaku Oxford Diffraction). Using Olex2³ the structures were solved with the ShelXT⁴ structure solution program using Intrinsic Phasing and refined with ShelXL⁴ using least-square minimization. Compound **3a** co-crystallized with two independent molecules in the asymmetric unit and seven of the eight CF3 moieties were found to be disordered and refined on 2 sites with occupation factors equal to 0.8 and 0.2 respectively. For **4** the terminal part of one octylamin moiety was found to be disordered and refined on two sites with occupation factors equal to 0.5. In both structures all H-atoms except those of the disordered octylamin for **4** were found experimentally and were refined with riding coordinates to their parent atoms and their Uiso parameters constraint to 1.2Ueq(parent atoms) for the CH, CH₂, NH and NH₂ and 1.5Ueq(parent atoms) for the CH₃.

Electrochemistry. Cyclic voltammetry (CV) data were recorded using a BAS 100 (Bioanalytical Systems) potentiostat and the BAS100W software (v2.3). All the experiments were conducted under an argon atmosphere in a standard one-compartment using a three electrodes setup: a Pt working electrode ($\emptyset = 1.6 \text{ mm}$), a Pt counter electrode and an Ag/AgCl reference electrode (filled with a 3 M NaCl solution). Tetra-n-butylammonium hexafluorophosphate ([TBA][PF₆]) was used as supporting electrolytes (10⁻¹ M), with a concentration of the electro-active compound *ca*. 10⁻³ M. The reference electrode was calibrated using ferrocene (E°(Fc/Fc⁺) = 0.46V/SCE (DCM), 0.46V/SCE (DMF)).⁵ The scan rate was 100 mV/S. Before experiment, the solution was degassed using argon and the working electrode (Pt) was polished before each recording.

Vapochromism. Indium Tin Oxide coated glass (ITO, 30 mm x 20 mm) was ozonized for 15 min in a Novascan[®] PSD pro series-Digital UV-Ozone system. A solution of **3a** in dichloromethane (0.3 M) was prepared and 10 wt. % of polyvinylpyrrolidone (PVP, average MW = 55,000 Da) were added. 300 μ L of solution were deposited on ITO surface before rotation at 1000 rpm for 1 min in a Laurell[®] Model WS-650MZ-23NPP spin coater. The thin film was dried under vacuum for 1 h before use. A 320 mL glass tank was filled with 7 vials (5mL) and 1 mL of solvent was distributed uniformly between the 7 vials. The glass tank was kept closed during 1 h before the beginning of the vapochromism experiment. The ITO sample was placed face down inside the glass tank with the help of a support (see Figure S 44). Once significant color change was visually found, the absorption spectra of the thin layer were recorded on a Vary[®] Cary 5000.

S-II. SYNTHETIC PROTOCOLS AND CHARACTERIZATIONS

Compound 5: 4,6-dinitro-N¹,N³-bis(4-(trifluoromethyl)phenyl)benzene-1,3-diamine



1,5-difluoro-2,4-dinitrobenzene (4 g, 21.8 mmol, 1 equiv.), 4-(trifluoromethyl)aniline (7.38 g, 45.8 mmol, 2.1 equiv.) and *N,N*diisopropylethylamine (11.36 mL, 65.4 mmol, 3 equiv.) were heated at 140 °C for 2 hours in a pressure tube. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed several times with ethanol and dried under vacuum to afford the product as an orange solid (8.41 g, 78%). ¹H NMR (CDCI₃, 400 MHz): δ = 9.82 (br s, 2H, NH), 9.34 (s, 1H, CH), 7.64 (d, *J* = 8.5 Hz, 4H, CH), 7.28 (d, *J* = 8.5 Hz, 4H, CH), 6.52 (s, 1H, CH). ¹³C NMR (101 MHz, DMSO): δ = 145.7 (C), 142.6 (C), 128.5 (CH), 127.0 (CH), 126.7

(C), 126.2 (q, J = 32 Hz), 125.5 (CH), 124.5 (q, J = 274 Hz), 123.1 (C), 99.3 (CH). **IR (neat, cm⁻¹):** v = 3350, 3095, 2094, 2003, 1630, 1601, 1563, 1515, 1403, 1316, 1287, 1228, 1162, 1101, 1062, 1013, 930, 871, 829, 740, 764, 697. **HRMS (ESI+)** calculated for [M+H]⁺: 487.0836 (C₂₀H₂₃F₁₆N₄O₄⁺), found 487.0837.

Compound 1: (*E*)-6-imino- N^1 -(4-(trifluoromethyl)phenyl)-3-((4-(trifluoromethyl)phenyl)imino) cyclohexa-1,4-diane-1,4-diamine



Compound **5** (150 mg, 0.31 mmol, 1 equiv.) was dissolved in 20 mL of EtOH. The solution was added by Pd/C (5 wt.%, 10 mg, 0.003 mmol, 0.01 equiv.), hydrazine monohydrate (145 μ L, 4.62 mmol, 15 equiv.) and was stirred at reflux for 3 h. The reaction mixture was evaporated, the residue dissolved in MeOH, K₂CO₃ (212 mg, 1.54 mmol, 5 equiv.) was added and the solution was stirred 2 h at room temperature. The reaction mixture was filtered on Celite[®] and the filtrate was evaporated. The residue dissolved in dichloromethane and washed with H₂O

and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated to afforded **1** as an red solid (84 mg, 64 %). ¹H NMR (400 MHz, DMSO): δ = 7.94 (br s, 4H, NH), 7.61 (d, *J* = 8.4 Hz, 4H, CH), 7.16 (d, *J* = 8.4 Hz, 4H, CH), 5.78 (s, 1H, CH), 5.70 (s, 1H, CH). ¹³C NMR (101 MHz, DMSO): no ¹³C NMR spectrum could be recorded owing to the poor solubility. **IR (neat, cm⁻¹):** v = 3350, 3095, 2094, 2002, 1630, 1601, 1563, 1516, 1489, 1403, 1316, 1287, 1228, 1163, 1101, 1062, 1013, 930, 871, 829, 740, 764, 697. **HRMS (ESI+)** calculated for [M+H]⁺: 425.1195 (C₂₀H₁₅N₄F₆⁺), found 425.1197.

Compound 6: 4,4'-((4,6-dinitro-1,3-phenylene)bis(azanediyl))dibenzonitrile



1,5-difluoro-2,4-dinitrobenzene (1 g, 4.90 mmol, 1 equiv.), 4-aminobenzonitrile (1.447 g, 12.25 mmol, 2.5 equiv.) and *N*,*N*-diisopropylethylamine (5.12 mL, 29.40 mmol, 6 equiv.) were heated at 140 °C for 2 hours in a pressure tube. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed several times with ethanol and dried under vacuum to afford the product as an orange solid (1.580 g, 81%). ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 9.90 (br s, 2H, NH), 9.00 (s, 1H, CH), 7.91 (d, *J* = 8.5 Hz, 4H, CH), 7.52 (d, *J* = 8.5 Hz, 4H, CH),

6.64 (s, 1H, CH). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 143.9 (C), 142.9 (C), 133.6 (CH), 127.8 (CH), 127.2 (C), 123.3 (CH), 118.7 (C), 106.7 (C), 101.0 (CH). IR (neat, cm⁻¹): v = 3307, 2217, 2115, 1921, 1795, 1626, 1566, 1527, 1498, 1424, 1403, 1343, 1297, 1228, 1168, 922, 827, 737, 702. HRMS (ESI+) calculated for [M+NH₄]⁺: 418.1258 (C₂₀H₁₆N₇O₄⁺), found: 418.1262.

Compound 8: 4,4'-((4,6-diamino-1,3-phenylene)bis(azanediyl))dibenzonitrile dihydrochloride



In a pressure bomb, compound **6** (1 g, 2.50 mmol, 1 equiv.) and SnCl₂•2H₂O (5.636 g, 24.98 mmol, 10 equiv.) were dissolved in 30 mL of concentrated HCl (12 N) and 50 mL of dichloromethane. The bomb was closed with a Teflon seal and the mixture was stirred at 45 °C for 2 days. The resulting precipitate was filtered, washed several times with HCl (12 N), then Et₂O and finally dried under vacuum to afford the product as an orange powder (968 mg, 94%). The compound was stored at -4 °C to prevent its oxidation to the corresponding quinone. ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 9.15 (br s, 2H, NH), 7.64 (d, *J* = 8 Hz, 4H, CH), 7.49 (s,

1H, CH), 7.26 (s, 1H, CH), 6.98 (d, J = 8 Hz, 4H, CH), 5.74 (br s, 6H, NH). ¹³C NMR (DMSO-*d*₆, 100 MHz): No ¹³C NMR spectrum could be recorded owing to the poor stability in solution. HRMS (ESI+) calculated for [M+H]⁺: 341.1509 (C₂₀H₁₇N₆⁺), found: 341.1507.

Compound 2a: (*E*)-4-((4-amino-3-((4-cyanophenyl)imino)-6-iminocyclohexa-1,4-dien-1-yl)amino) benzonitrile



Compound **8** (500 mg, 0.21 mmol, 1 equiv.) was dissolved in 50 mL of absolute ethanol. The solution was added by K_2CO_3 (836 mg, 6.05 mmol, 5 equiv.) and the solution was stirred at 25 °C and under aerobic conditions for 20 h. The reaction mixture was evaporated and the residue was washed several times with water and Et₂O, and finally dried under reduced pressure to afford the product as an orange-red powder (314 mg, 77%). ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 8.10 (br s, 4H, NH),

2a 7.72 (d, J = 6.7 Hz, 4H, CH), 7.12 (d, J = 6.7 Hz, 4H, CH), 5.80 (s, 1H, CH), 5.66 (s, 1H, CH). ¹³C NMR (DMSO-*d*₆, 100 MHz): $\delta = 155.5$ (C), 151.3 (C), 148.9 (C), 133.1 (CH), 121.5 (CH), 119.3 (C), 104.0 (C), 95.2 (CH), 90.9 (CH). IR (neat, cm⁻¹): v = 3458, 3341, 3204, 2222, 1681,

1637, 1597, 1556, 1506, 1402, 1288, 1244, 1223, 1175, 1104, 917, 854, 825, 725. **HRMS (ESI+)** calculated for $[M+H]^+$: 339.1353 ($C_{20}H_{15}N_{3}^+$), found: 339.1349.

Compound 2b: (*E*)-4-((5-((4-cyanophenyl)amino)-4-imino-2-(octylamino)cyclohexa-2,5-dien-1-ylidene)amino)benzonitrile



Compound **2a** (50 mg, 0.148 mmol, 1 equiv.) was dissolved in 15 mL of *N*,*N*dimethylformamide. The solution was added by *n*-octylamine (49 μ L, 0.296 mmol, 2 equiv.) and the solution was stirred at 25 °C for 16 h. The reaction mixture was evaporated, the residue dissolved in dichloromethane and washed with an aqueous saturated solution of NH₄Cl and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. Purification by column chromatography over silicagel using dichloromethane/ethyl acetate (9:1) as eluent afforded the product as an orange solid (21 mg, 31%). **R**_f: 0.41 (SiO₂,

dichloromethane/ethyl acetate, 9:1). ¹H NMR (DMSO-*d*₆, 400 MHz): $\delta = 7.79$ (d, J = 8.5 Hz, 2H, CH), 7.71 (d, J = 8.6 Hz, 4H, CH), 7.22 (d, J = 8.6 Hz, 4H, CH), 7.10 (d, J = 8.5 Hz, 4H, CH), 5.84 (s, 1H, CH), 5.77 (s, 1H, CH), 3.41 (t, J = 7.2 Hz, 2H, N-CH₂), 1.66 (quint, J = 7.2 Hz, 2H, CH₂), 1.35 – 1.22 (m, 10H, CH₂), 0.85 (t, J = 6.9 Hz, 6H, CH₃). ¹³C NMR (DMSO-*d*₆, 100 MHz): $\delta = 152.6$ (C), 133.2 (CH), 133.1 (CH), 121.6 (CH), 120.8 (CH), 119.2 (C), 119.1 (C), 105.1 (C), 104.0 (C), 92.0 (CH), 29.6 (CH), 48.3 (NCH₂), 31.2 (CH₂), 29.8 (CH₂), 28.8 (CH₂), 28.7 (CH₂), 27.0 (CH₂), 22.0 (CH₂), 13.9 (CH₃). Missing quaternary carbons due to highly resonant structure. **IR (neat, cm⁻¹):** v = 3464, 3344, 3068, 2917, 2849, 2225, 1618, 1599, 1561, 1511, 1467, 1419, 1352, 1319, 1255, 1237, 1209, 1176, 1102, 1014, 910, 845, 817, 719, 683. **HRMS (ESI+)** calculated for [M+H]⁺: 451.2605 (C₂₈H₃₁N₆⁺), found: 451.2603.

Compound 2c: 4-((E)-((E)-5-((4-cyanophenyl)amino)-2-(octylamino)-4-(octylimino)cyclohexa-2,5-dien-1-ylidene)aminobenzonitrile



Compound **2a** (50 mg, 0.148 mmol, 1 equiv.) was dissolved in 14 mL of *N*,*N*dimethylformamide. The solution was added by *n*-octylamine (194 μ L, 1.182 mmol, 8 equiv.) and the solution was stirred at 25 °C for 63 h. The reaction mixture was evaporated, the residue dissolved in dichloromethane and washed with an aqueous saturated solution of NH₄Cl and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. Purification by column chromatography over silicagel using dichloromethane/ethyl acetate (95:5) as eluent afforded the product as an orange solid (60 mg, 72%). **R**_f: 0.90 (SiO₂,

dichloromethane/ethyl acetate, 95:5). ¹H NMR (Acetone- d_6 , 400 MHz): δ = 7.77 (br s, 1H, NH), 7.72 (d, J = 8.5 Hz, 4H, CH), 7.20 (d, J = 8.5 Hz, 4H, CH), 6.02 (s, 1H, CH), 5.65 (s, 1H, CH), 3.43 (t, J = 7.1 Hz, 4H, N-CH₂), 1.75 (quint, J = 7.2 Hz, 4H, CH₂), 1.46 – 1.30 (m, 20H, CH₂), 0.88 (t, J = 7.0 Hz, 6H, CH₃). ¹³C NMR (Acetone- d_6 , 100 MHz): δ = 151.4 (C), 151.2 (C), 150.8 (C), 135.2 (CH), 122.9 (CH), 120.6 (C), 107.8 (C), 93.9 (CH), 87.8 (CH), 48.1 (NCH₂), 33.6 (CH₂), 31.4 (CH₂), 31.2 (CH₂), 31.0 (CH₂),

29.2 (CH₂), 24.3 (CH₂), 15.4 (CH₃). **IR (neat, cm⁻¹):** v = 3359, 3263, 2922, 2852, 2220, 1597, 1561, 1510, 1465, 1348, 1312, 1238, 1175, 924, 795, 721. **HRMS (ESI+)** calculated for [M+H]⁺: 563.3857 (C₃₆H₄₇N₆⁺), found: 563.3856.

Compound 3a: (*E*)-*N*¹-(3,5-bis(trifluoromethyl)phenyl)-3-((3,5-bis(trifluoromethyl)phenyl)imino)-6-iminocyclohexa-1,4-diane-1,4-diamine



Compound **7** (200 mg, 0.321 mmol, 1 equiv.) was dissolved in 40 mL of EtOH. The solution was added by Pd/C (5 wt.%, 34 mg, 0.016 mmol, 0.05 equiv.), hydrazine monohydrate (233 mg, 4.815 mmol, 15 equiv.) and was stirred at reflux for 2 h. The reaction mixture was evaporated and the residue dissolved in MeOH. K_2CO_3 (222 mg, 1.6 mmol, 5 equiv.) was added and the solution was stirred 2 h at 25 °C. The reaction

mixture was filtered on Celite[®] and the filtrate was evaporated. The residue was dissolved in dichloromethane and washed with H₂O and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated to afforded **3a** as a red solid (170 mg, 84 %). ¹H NMR (400 MHz, CDCI₃): δ = 7.54 (s, 2H, CH), 7.33 (s, 4H, CH), 6.95 (br s, 2H, NH), 5.85 (s, 1H, CH), 5.70 (s, 1H, CH). ¹³C NMR (101 MHz, DMSO): δ = 158.3 (C), 151.2 (C), 150.2 (C), 130.8 (q, J = 33 Hz, C), 123.2 (q, *J* = 273 Hz, C), 121.4 (CH), 114.5 (CH), 92.4 (CH), 85.9. (CH). IR (neat, cm⁻¹): v = 3389, 3266, 2923, 2853, 2109, 1646, 1577, 1528, 1472, 1370, 1274, 1169, 1117, 999, 953, 873, 845, 699, 681. HRMS (ESI+) calculated for [M+H]⁺: 561.0943 (C₂₂H₁₃N₄F₁₂⁺), found 561.0946.

Compound 3b: $(3E,6E)-N^1-(3,5-bis(trifluoromethyl)phenyl)-3-((3,5-bis(trifluoromethyl)phenyl)imino)-N4-octyl-6-(octylimino)cyclohexa-1,4-diame-1,4-diamine$



Compound **3a** (25 mg, 0.045 mmol, 1 equiv.) was dissolved in 1.5 mL of methanol. The solution was added by *n*-octylamine (59 μ L, 0.357 mmol, 8 equiv.) and stirred at 25 °C for 80 h. The reaction mixture was evaporated and the residue was purified by column chromatography over silicagel plug using dichloromethane as eluent afforded the product as an orange solid (24.4 mg, 70%).

3b $R_f = 0.66$ (SiO₂, dichloromethane). ¹H NMR (400 MHz, CDCI₃): $\delta = \delta = 7.51$ (s, 2H, CH), 7.32 (s, 4H, CH), 5.77 (s, 1H, CH), 5.47 (s, 1H, CH), 3.37 (t, J = 7.1 Hz, 4H, N-CH₂), 1.76 (quint, J = 7.2 Hz, 4H, CH₂), 1.52 – 1.16 (m, 20H, CH₂), 0.89 (t, J = 7.0 Hz, 6H, CH₃). ¹³C NMR (101 MHz, CDCI₃): $\delta = 149.7$ (C), 148.9 (C), 146.6 (C), 132.6 (q, J = 34 Hz, C), 123.1 (q, J = 273 Hz, C), 120.3 (CH), 116.6 (CH), 90.4 (CH), 86.1 (CH), 46.6 (CH₂), 31.8 (CH₂), 29.7 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 27.5 (CH₂), 22.7 (CH₂), 14.1 (CH₃). **IR (neat, cm⁻¹):** v = 3380, 2928, 2857, 2121, 20.5 (CH₂) = 2.5 (CH₂).

1605, 1575, 1509, 1472, 1370, 1274, 1168, 1126, 954, 885, 846, 797, 701, 682. **HRMS (ESI+)** calculated for [M+H] ⁺: 785.3447 (C₃₈H₄₅F₁₂N₄⁺), found 785.3453.

Compound 4: (3E, 6E)- N^{1} -(5-fluoro-2, 4-dinitrophenyl)-3-((5-fluoro-2, 4-dinitrophenyl))imino)- N^{4} -octyl-6-(octylimino)cyclohexa-1,4-diane



To a solution of **9** (100 mg, 0.137 mmol, 1 equiv.) in 2 mL of degassed chloroform was added 2,3-dichloro-5,6-dicyano-1,4benzoquinone (31 mg, 0.137 mmol, 1 equiv.) and the mixture was stirred at 25 °C for 30 minutes. After concentration under reduced pressure, the crude residue was purified by column chromatography over silicagel using dichloromethane as eluent to afford the product as a green solid (67 mg, 67%). **R**_f: 0.80 (SiO₂, dichloromethane). ¹**H NMR (CDCI₃, 400 MHz):** δ = 8.80 (d, *J*_{*H*-*F*} = 7.7 Hz, 2H, CH), 8.50 (br

s, 2H, NH), 6.9 (d, $J_{H-F} = 12.1$ Hz, 2H, CH), 5.42 (s, 1H, CH), 5.36 (s, 1H, CH), 3.44 (t, J = 7.1 Hz, 8H, N-CH₂), 1.81 (quint, J = 7.2 Hz, 8H, CH₂), 1.54 – 1.28 (m, 20H, CH₂), 0.89 (t, J = 7.0 Hz, 6H, CH₃). ¹³**C NMR (CDCI₃, 100 MHz):** $\delta = 158.1$ (C, $J_{C-F} = 273$ Hz), 156.0 (C), 151.2 (C, $J_{C-F} = 6$ Hz), 149.5 (C), 137.2 (C), 130.0 (C, $J_{C-F} = 8$ Hz), 125.4 (CH), 111.3 (CH, $J_{C-F} = 23$ Hz), 87.8 (CH, $J_{C-F} = 7$ Hz), 83.9 (CH), 44.3 (N-CH₂), 31.7 (2 CH₂), 29.1 (2 CH₂), 28.4 (CH₂), 27.0 (CH₂), 22.6 (CH₂), 14.1 (CH₃). **IR (neat, cm⁻¹):** v = 3282, 3104, 2923, 2854, 2109, 2001, 1739, 1584, 1610, 1506, 1457, 1329, 1281, 1208, 1125, 1040, 907, 869, 816, 737, 688. **HRMS (ESI+)** calculated for [M+H]⁺: 729.3166 (C₃₄H₄₃F₂N₈O₈⁺), found: 729.3166.

S-III. ¹H AND ¹³C NMR SPECTRA



Figure S 1. ¹H NMR (400 MHz, CDCl₃) of compound **5**.



Figure S 2. ¹³C NMR (101 MHz, DMSO) of compound **5**.



Figure S 3. ¹H NMR (400 MHz, DMSO-*d*₆) of compound **1**.



Figure S 4. ¹H NMR (400 MHz, DMSO-*d*₆) of compound **6**.



Figure S 5. ¹³C NMR (101 MHz, DMSO-*d*₆) of compound **6**.



Figure S 6. ¹H NMR (400 MHz, DMSO-*d*₆) of compound **8**.



Figure S 7. ¹H NMR (400 MHz, DMSO-*d*₆) of compound **2a**.



Figure S 8. ¹³C NMR (101 MHz, DMSO-*d*₆) of compound **2a**.



Figure S 9. ¹H NMR (400 MHz, DMSO-*d*₆) of compound **2b**.



Figure S 10. ¹³C NMR (101 MHz, DMSO-*d*₆) of compound **2b**.



Figure S 11. ¹H NMR (400 MHz, Acetone-*d*₆) of compound **2c**.



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm (t1)

Figure S 12. ¹³C NMR (101 MHz, Acetone-*d*₆) of compound **2c**.



Figure S 13. ¹H NMR (400 MHz, CDCl₃) of compound **3a**.



Figure S 14. ¹³C NMR (101 MHz, DMSO-*d*₆) of compound **3a**.



Figure S 15. ¹H NMR (400 MHz, CDCl₃) of compound **3b**.



Figure S 16. ¹³C NMR (101 MHz, CDCl₃) of compound **3b**.



Figure S 17. ¹H NMR (400 MHz, CDCl₃) of compound **4**.



Figure S 18. ¹³C NMR (101 MHz, CDCl₃) of compound **4**.

S-IV. SINGLE CRYSTAL X-RAY DIFFRACTION

Compound	3a	4
Formula	$C_{22}H_{12}F_{12}N_4$	$C_{34}H_{42}F_2N_8O_8$
Mw	530.36	728.75
Crystal system	monoclinic	monoclinic
Measurement temperature/ K	293	293
Space group	P 2 ₁ /c	P 21/n
a/ Å	15.8769(2)	9.05337(2)
b/ Å	17.4704(2)	17.8869(4)
c/ Å	16.9020(2)	22.6505(4)
β/ °	101.4090(10)	92.648(2)
V/ Å ³	4595.57(10)	3664.16(13)
Z	8	4
Dc/g.cm ⁻³	1.62	1.321
Crystal colour	orange	brown
Crystal size/mm ³	0.03*0.22*0.5	0.02*0.14*0.26
μ(Mo-Kα)/mm ⁻¹	1.506	0.862
N° of refl. measured	33093	36478
N° of unique refl.	8752	7011
N° of observed refl.[F ² > 4σ F ²]	7519	5254
N° parameters refined	850	478
R ₁ [F ² >4σF ²]	0.0815	0.0727
wR ₁ [F ² >4σF ²]	0.02315ª	0.2032 ^b
R ₂ [all refl.]	0.0882	0.0930
wR ₂ [all refl.]	0.2431	0.2245
Goodness of fit [all refl.]	1.051	1.029
Residual Fourier/e. Å ⁻³	-0.76; 0.63	-0.44; 0.44

^a w=1/[$\sigma^2(Fo^2)$ +(0.1655P)²+1.8508P] where P=(Fo²+2Fc²)/3 ^b w=1/[$\sigma^2(Fo^2)$ +(0.1125P)²+2.4762P] where P=(Fo²+2Fc²)/3

S-V. ELECTRONIC ABSORPTION



Figure S 19. Absorption solvatochromism of compounds 1-4.



Figure S 20. pH-dependent absorption spectra of compound 1.



Figure S 21. pH-dependent absorption spectra of compound 2a.



Figure S 22. pH-dependent absorption spectra of compound 2b.



Figure S 23. pH-dependent absorption spectra of compound **2c**.



Figure S 24. pH-dependent absorption spectra of compound 3a.



Figure S 25. pH-dependent absorption spectra of compound 3b.



Figure S 26. pH-dependent absorption spectra of compound 4.

S-VI. CYCLIC VOLTAMMETRY

Compound	Solvent	E _{1/2} red2	E _{1/2} red1	E _{1/2} ox	ΔE
1	DCM	-	-1.41	0.32	1.63
1	DMF	-	-1.42	0.10	1.52
2a	DCM	-	-1.33	0.32	1.65
2a	DMF	-	-1.29	0.15	1.44
2b	DCM	-	-1.42	0.34	1.76
2b	DMF	-	-1.32	0.20	1.52
2c	DCM	-	-1.65	0.33	1.98
2c	DMF	-	-1.42	0.21	1.63
3a	DCM	-	-1.29	0.44	1.73
3a	DMF	-1.75	-1.25	0.24	1.49
3b	DCM	-	-1.67	0.42	2.09
3b	DMF	-2.12	-1.40	0.28	1.68
4	DCM	-1.41	-0.83	0.65	1.48
4	DMF	-1.36	-0.79	0.50	1.29

Table S 1. Half-wave potential (V vs. Fc/Fc⁺) of the compounds (recorded in solutions containing 0.1 M of $[(nBu_4N)PF_6]$ at a scan rate of 100 mV s⁻¹).



Figure S 27. Cyclic voltammograms of compound 1 in DCM (left) and DMF (right).



Figure S 28. Cyclic voltammograms of compound 2a in DCM (left) and DMF (right).



Figure S 29. Cyclic voltammograms of compound 2b in DCM (left) and DMF (right).



Figure S 30. Cyclic voltammograms of compound 2c in DCM (left) and DMF (right).



Figure S 31. Cyclic voltammograms of compound 3a in DCM (left) and DMF (right).



Figure S 32. Cyclic voltammograms of compound **3b** in DCM (left) and DMF (right).



Figure S 33. Cyclic voltammograms of compound 4 in DCM (left) and DMF (right).

S-VII. Theoretical calculations

Methods. All calculations have been made with Gaussian16,⁶ using default procedures and algorithms except when noted below. We have used the PBE0⁷ hybrid functional for all our calculations, and applied tighten thresholds for the energy (at least 10⁻⁹ au) and geometry convergences (so-called tight threshold in Gaussian), as well as used an improved DFT integration grid (ultrafine grid). For all compounds, we have optimized the ground-state geometry with the 6-311++G(2d,2p) atomic basis set and subsequently verified the absence of imaginary frequencies by computing analytically the Hessian at the same level of theory. The excited-state calculations were performed with TD-DFT considering 15 states determined with the same functional and atomic basis set. The solvent effects were modeled through the well-known Polarizable Continuum Model (PCM),⁸ using the linear-response nonequilibrium model for the excited-state calculations. We recall that PCM is an implicit solvation model, i.e., the solvent is modeled as a structureless continuum defined by macroscopic parameters, e.g., a uniform dielectric constant. PCM can therefore account for polarization effects but not for specific interactions between the dye and the solvent molecules, e.g., hydrogen bonds. This model is therefore valid when considering aprotic solvents such as dichlroromethane and dimethylsulfoxide. The density difference plots representing the excited states have been drawn by computing the excited state density with the Z-vector approach. Charge-transfer (CT) parameters were determined using Le Bahers' model.⁹ As we found that the lowest excited-state of the zwitterionic form present a CT character, we have also computed these CT parameters as well as the absorption spectra using the range-separated hybrid CAM-B3LYP functional¹⁰ and similar outcomes were found (vide infra). Partial atomic charges were computed at the PCM-PBE0 level using the Merz-Kollman partitioning. To estimate the aromaticity, we determined the so-called Nucleus Independent Chemical Shifts (NICS) in gas phase using the B3LYP/6-311+G(d,p) model, that is standard for such calculations.¹¹

Study of 2a. For **2a**, we performed a full conformational and tautomeric search. Four tautomeric structures can be envisaged (see Figure S 34A). For all of them, one can foresee two possible rotamers, depending on the relative orientations of the *p*-cyano-phenyl ring (see Figure S 34B) leading to C_s -like and C_2 -like symmetries for the final structures. The computed free energies of these structures are listed in Table S 2. As expected from chemical intuition, we note that: i) the **A** and **X** tautomers are much less stable than the **Z** and **Q** structures, irrespective of the medium; ii) for a given tautomer, the two rotamers present very similar energies and likely co-exist in solution; and iii) increasing the polarity of the medium leads to a relative improvement of the stability of the **Z** tautomers. Indeed, in gas-phase, the Boltzmann distribution indicates there should be a totally negligible amount of zwitterions (**Q** form weight of 99.99%) whereas in DCM and DMSO, the ratio of **Z** tautomers attain 5% and 14%, respectively. Of course, with the very small DFT energy differences displayed in Table S 2, these estimates come with significant error bars. There is nevertheless a clear trend that nicely fits the experimental data: increasing the polarity of the medium stabilizes the zwitterionic form.



Figure S 34. Left: representation of the different tautomers of **2a**. Right: representation of the possible rotamers for the Z tautomer.

Table S 2. Relative free energies of the different forms of **2a** computed for the structures displayed in Figure S 34. All results are given in kcal.mol⁻¹, considering the most stable structure as reference.

Tautomer	Rotamer	Gas	DCM	DMSO
Z	C _s -like	5.5	1.4	0.8
	C ₂ -like	5.9	2.3	1.5
Q	C _s -like	0.1	0.0	0.0
	C ₂ -like	0.0	0.1	0.0
А	C _s -like	18.0	17.8	16.8
	C ₂ -like	18.2	17.5	17.3
X	C _s -like	18.6	13.6	12.0
	C ₂ -like	13.2	9.7	9.0

We have used TD-DFT to determine the spectral properties of the different species. For the **Z** and **Q** structures, the computed spectra are displayed in Figure S 35 (in DMSO) and S 36 (in DCM), respectively, together with the density difference plots corresponding to the lowest relevant excited states. For a given tautomer, PCM-TD-PBE0 calculations return essentially the same vertical excitation energies and oscillator strengths in both solvents, so that the experimentally observed differences in the UV-Vis absorption spectra are indeed related to different ratio of the tautomers in solution rather than a "direct" solvatochromic effect. Table S 3 lists the computed transition energies, oscillator strength and MO compositions for the two tautomers of **2a** in DCM. These MOs are represented in Figure S 37.



Figure S 35. Computed PCM(DMSO)-TD-XCF/6-311++G(2d,2p) with XCF=PBE0 (full lines) and XCF=CAM-B3LYP (dotted line) spectra of the **Z** tautomer of **2a** (C_s -like conformation) using a broadening Gaussian with a HWHM (half-width at half-maximum) of 2500 cm⁻¹. The density difference plots for the lowest excited states obtained with the PBE0 functional are shown as well on the right hand side (isovalue: 0.0014 au). The red and blue areas indicate increase and decrease of the electron density upon absorption, respectively.



Figure S 36. Computed PCM(DCM)-TD-PBE0/6-311++G(2d,2p) spectra of the **Q** tautomer of **2a** (C_s -like conformation). See caption of Figure S 35.

Table S 3. Relevant excited states computed for the C_s -like rotamers of **Z** and **Q** of **2a** in DCM. We report the computed absorption wavelength (in nm), oscillator strength and dominating MO composition (H=HOMO; L=LUMO). Only excited states showing significant oscillator strengths have been listed. The MO diagrams for the two structures are displayed in Figure S 37.

Tautomer	State	Wavelength	f	MO composition
	1	694	0.17	H to L (99%)
	2	435	0.14	H-1 to L (94%)
7	3	400	0.16	H-2 to L (91%)
Z	4	349	0.20	H to L+1 (95%)
	5	344	0.25	H to L+2 (97%)
	6	331	0.24	H-3 to L (85%)
	1	498	0.06	H to L (95%)
	2	398	0.37	H-1 to L (79%), H-2 to L (16%)
	3	359	0.25	H-2 to L (78%), H-1 to L (16%)
Q	4	308	0.30	H to L+1 (96%)
	5	297	0.12	H to L+2 (93%)
	9	281	0.31	H-3 to L (41%), H-4 to L (22%), H-6 to L (14%)
	10	276	0.14	H-1 to L+1 (91%)
Q	1 2 3 4 5 9 10	498 398 359 308 297 281 276	0.06 0.37 0.25 0.30 0.12 0.31 0.14	H to L (95%) H-1 to L (79%), H-2 to L (16%) H-2 to L (78%), H-1 to L (16%) H to L+1 (96%) H to L+2 (93%) H-3 to L (41%), H-4 to L (22%), H-6 to L (14%) H-1 to L+1 (91%)



Figure S 37. MO diagrams for the Z (left) and Q (right) structures of 2a that are detailed in Table S 3. The energies of the MO are given in eV. Dark (light) colored bars corresponding to virtual (occupied) MO.

The aromaticity of all cycles of **2a** have been estimated through the use of the well-known NICS(0) parameters. The results are displayed in Figure S 38. As expected the two *p*-CN-phenyl rings are always strongly aromatic, with NICS ranging from -7.3 to -8.3 ppm, similar to the value obtained for benzene with the same level of theory (-8.0 ppm).⁹ In contrast, the tetra-amino cycle is always antiaromatic (positive NICS), with values that are similar for **Z** and **Q**. In Figure S 39, we show the computed ESP charges computed for the different moieties of the same two tautomers. Interestingly, in the **Z** structure, the formally positive cyanine chain (in blue) bears a +0.50 e charge whereas the negative moiety bears a -0.34 e charge, the two *p*-CN-phenyls each bear a -0.08 e charge. In other words, the charge separation between the *upper* and *lower* parts of the molecule attains 1.00 electron [+0.50 - (-0.34+2x-0.16)] instead of the two electrons expected from the Lewis structure. In the **Q** form, this charge separation is close to zero (0.10 e), as expected.



Figure S 38. Computed NICS(0) values in ppm for the three cycles of the C_{s} -like Z and Q tautomers of 2a.



Figure S 39. Computed Merz-Kollman charges borne by different moieties of the C_s -like Z and Q tautomers of 2a. The central dashed line indicates the separation of the molecules into two halves, consistently with the coupling principle.

To further probe the nature of the lowest excited state of the **Z** tautomer of **2a**, we have performed several calculations: i) we have computed CT parameters using Le Bahers' model; ii) we have computed the partial atomic charges in the S_1 excited-state; iii) we have computed the NICS on the lowest triplet excited-state - which is generally viewed as very similar to the lowest singlet in terms of electron density; and iv) we have optimized the geometry of the lowest triplet excited-state (T_1). Some key results are displayed in Figure S 40. With Le Bahers' model, we obtain that the zwitterionic band at *ca*. 700 nm is characterized by a quite strong charge-transfer character (given the size of the molecule). Indeed, this

model predicts a transfer of 0.54 e charge over 1.87 Å,¹ *i.e.*, there is a significant CT from the negatively charged to the positively charge moieties upon absorption of light by the **Z** form of **2a**, which is in line with the reduction of the dipole moment from 23.1 to 18.3 D upon absorption (see main text). The MK partial atomic charges (Figure S 40, left) are consistent with the CT character of the lowest band, as the charge separation between the two halves of the **2a** is only 0.5 e in the lowest excited-state, that is *ca*. half of the charge separation obtained in the ground state for the **Z** form (*vide supra*). The calculation of the NICS of *T*₁ show that the central cycle is now slightly aromatic (-1.0 ppm, see Figure S 40 middle), indicating that the electronic transition induces a strong reduction of the anti-aromatic character of **2a**. For the ground state of the **Z** form of **2a**, we obtained a geometry very similar to the one of Figure 3 in the main text, with two independent cyanines separated by single bonds. In the lowest triplet state, that is used here as a model of *S*₁,² one notices limited elongations of the CC bonds involved in the two cyanines (from 1.385 to 1.388 Å, and from 1.399 to 1.409 Å), but a strong shortening (from 1.496 to 1.439 Å) of the central bonds that now gain a partial double bond character. This is consistent with the density difference plot of Figure S 35.

All these elements clearly point out that photon absorption at ca. 700 nm decrease the zwitterionic character of **2a** as a result of the significant CT between the two cyanines composing **2a**.



Figure S 40. Studies performed for the lowest excited-state of the **Z** form of **2a**. From left to right: partial atomic charges in the lowest S_1 state; NICS(0) computed considering the lowest triplet state ; optimized geometry of the ground and lowest triplet states in gas phase. Note that the C_s symmetry is used, and only non-equivalent bond lengths are given in Å.

¹ We are well aware the PBE0 might not be the most suited functional for estimating CT parameters. However, calculations with a range-sepatated hybrid, namely CAM-B3LYP, yield very similar trends, *i.e.*, a transferred charge of 0.58 e and a CT distance of 1.53 Å.

² When optimizing directly the geometry of S_1 , one obtains a very low transition energy (1.13 eV, *f*=0.07) indicating that single-reference methods like TD-DFT become inadequate, which is why we used the lowest triplet computed at the U-DFT level in the present analysis.

Study of pH effects for 2a. For studying protonation and deprotonation effects on 2a, we have first carried out, as for the neutral forms, a search for the possible tautomers and rotamers. Let us start by the mono-protonated structure, for which one can envisaged two possible tautomers, simply denoted *ZH* and *QH* (Figure S 41A). As can be seen in Table S 4, the former form, with a positive charge localized on the upper part is significantly more stable irrespective of the medium selected. Therefore in solution, we predict that only *ZH* is present. However, experimental protonation could also potentially lead to the doubly protonated form of 2a. For this structure there is one possible tautomer only (*ZH*₂ in Figure S 41B). We have therefore evaluated the spectra of both *ZH* and *ZH*₂ with TD-DFT. For the former, we obtained (after convolution, see below) a band peaking at 419 nm and a shoulder in the 500-650 nm region in DMSO, which is in very good agreement with the experimental spectra (the band in the UV-blue region peaking at 416 nm in the same solvent). In contrast, for *ZH*₂ TD-DFT returns a maximum at 454 nm, corresponding to a discrepancy of 0.25 eV, and a shoulder that is between 600-750 nm, that does not match experiment (see Figure 5). One can safely attribute the experimental spectra in TFA to the *ZH* structure. As discussed in the main text, there is also a good match between the experimental and theoretical overall band shape when considering *ZH*.



Figure S 41. Representation of the possible tautomers for: A) the mono-protonated; B) the di-protonated; C) the mono-deprotonated; D) the di-deprotonated forms of **2a**

Table S 4.	Relative	free	energies	of th	e different	mono	-protonated	forms	of 2a	computed	for	the s	structures
displayed ir	i Figure S	40. <i>I</i>	All results	are g	ven in kca	l.mol ⁻¹ ,	considering	the mo	ost sta	ble structur	e as	refe	rence.

Tautomer	Rotamer	Gas	DCM	DMSO
ZH	C _s -like	0.0	0.0	0.0
	C ₂ -like	0.7	0.6	0.2
QH	C _s -like	4.3	7.1	7.1
	C ₂ -like	4.6	7.7	7.9

The TD-DFT simulated spectra of **ZH** and **ZH**₂ are given in Figure S 42 and the main absorption band together with MO copositions is shown in Table S 5. The shoulder in the experimental spectra of Figure 5 at 550 nm corresponds to the absorption computed with TD-DFT at 575 nm for **ZH**. The density difference plot of the corresponding excited state, displayed in the right-hand-side of Figure S42, shows similitudes with the lowest state of the neutral **2a**, but for the change of sign of the contribution on the non-substituted nitrogen atom.



Figure S 42. Computed PCM(DMSO)-TD-PBE0/6-311++G(2d,2p) spectra of the **ZH** (sticks and full line) and **ZH**₂ (dotted line) tautomer of **2a+H**⁺ and **2a+2H**⁺ (C_s -like conformation) using a broadening Gaussian with a HWHM of 2500 cm⁻¹. The density difference plots for the lowest excited states of **ZH** are shown as well (isovalue: 0.0014 au). The red and blue areas indicate increase and decrease of the electron density upon absorption, respectively.

Tautomer	State	Wavelength	f	MO composition
	1	575	0.10	H to L (97%)
	2	460	0.14	H-1 to L (92%)
711	3	407	0.27	H-2 to L (94%)
20	6	309	0.34	H-5 to L (78%), H-6 to L (11%)
	7	290	0.32	H to L+1 (85%)
	8	283	0.18	H to L+2 (69%), H-6 to L (24%)
	1	650	0.06	H to L (92%)
74.	2	480	0.33	H-1 to L (90%)
ΖΠ2	3	429	0.30	H-2 to L (98%)
	6	432	0.13	H-5 to L (93%)

Table S 5. Relevant excited state computed for the C_s -like forms of ZH and ZH_2 in DMSO. We report the computed absorption wavelength (in nm), oscillator strength and dominating MO composition (H=HOMO; L=LUMO). Only excited states showing significant oscillator strengths have been reported.

For the de-protonated structure one can also design two possible tautomers, **ZB** and **QB** (Figure S 41C). As can be seen in Table S 6, the former form, with a negative charge localized on the lower part of the compound is more stable in all solvents. In this case, in contrast to the other structures, the C_s -like rotamers are also significantly more stable, irrespective of the medium selected. Therefore in solution, we predict that only **ZB** is present. As for the protonation, the possibility of the formation of the di-ion, **ZB**₂ (see Figure S 41D) was also considered and we have computed the TD-DFT spectra of both **ZB** and **ZB**₂. For the former, we obtained (after convolution, see below) two bands peaking at 576 nm and 381 nm in DMSO, which is is in very good agreement, in terms of both absolute and relative positions, with the experimental values of 608 nm and 379 nm in the same solvent. In contrast, for **ZB**₂ TD-DFT predicts maxima at 459 nm and 357 nm, which obviously does not fit at all the experiment (error > 0.5 eV for the long wavelength band).

Table S 6. Relative free energies of the different mono-protonated forms of **2a** computed for the structures displayed in Figure S 41. All results are given in kcal.mol⁻¹, considering the most stable structure as reference.

Tautomer	Rotamer	Gas	DCM	DMSO
ZB	C _s -like	0.0	0.0	0.0
	C ₂ -like	7.0	4.4	3.9
QB	C _s -like	12.3	9.8	9.7
	C ₂ -like	12.2	10.2	9.6

The TD-DFT simulated spectra of ZB and ZB_2 are given in Figure S 43 and the main absorption band together with MO copositions is shown in Table S 7.



Figure S 43. Computed PCM(DMSO)-TD-PBE0/6-311++G(2d,2p) spectra of the **ZB** (sticks and full line) and **ZB**₂ (dotted line) tautomer of **2a–H⁺** and **2a–2H⁺** (C_s -like conformation) using a broadening Gaussian with a HWHM of 2500 cm⁻¹. The density difference plots for the lowest excited states are shown as well (isovalue: 0.0014 au). The red and blue areas indicate increase and decrease of the electron density upon absorption, respectively.

Tautomer	State	Wavelength	f	MO composition
	1	576	0.20	H to L (99%)
ZB	2	397	0.48	H-1 to L (93%)
	4	367	0.31	H to L+1 (76%), H-2 to L (18%)
	2	464	0.57	H-1 to L (97%)
ZB ₂	4	386	0.12	H to L+3 (97%)
	8	351	0.46	H-1 to L+1 (71%), H-2 to L (20%)

Table S 7. Relevant excited state computed for the C_s -like forms of **ZB** and **ZB**₂ in DMSO. We report the computed absorption wavelength (in nm), oscillator strength and dominating MO composition (H=HOMO; L=LUMO). Only excited states showing significant oscillator strengths have been reported.

S-VIII. Vapochromism

1. In presence of DMF vapours



Figure S 44. Picture of the vapochromism setup using thin film of **3a** before (top left) and just after DMF exposure (top right).

2. In presence of DMSO vapours



Figure S 45. Absorption spectra of a PVP/**3a** film (1:9, wt/wt) on ITO substrate in presence of air and DMSO vapors (24 seconds interval between every black curves).

3. In presence of a mixture of toluene-DMF vapours

- Toluene/DMF (90:10): after 3 hours of exposure in the glass tank, the thin film becomes slightly brownish
- Toluene/DMF (80:20): the film becomes brownish after one hour and a half, then green after 14 hours, with partial degradation of the thin film
- Toluene/DMF (50:50): the film starts to turn green after 40 minutes exposure (see pictures Figure S 47, note that the aspect of the thin film is due to previous degradation during the toluene/DMF (80:20) experiment)



Figure S 46. Picture of the vapochromism setup using thin film of **3a** exposed to vapours of a toluene/DMF mixture (50:50).

S-IX. REFERENCES

1 L. Lavaud, Z. Chen, M. Elhabiri, D. Jacquemin, G. Canard and O. Siri, *Dalton Trans.*, 2017, **46**, 12794-12803.

2 Z. Chen, R. Haddoub, J. Mahé, G. Marchand, D. Jacquemin, J. Andeme Edzang, G. Canard, D. Ferry, O. Grauby, A. Ranguis and O. Siri, *Chem. Eur. J.*, 2016, **22**, 17820-17832.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

4 G. Sheldrick, Acta Crystallogr. A, 2015, 71, 3-8.

5 N. G. Connelly and W. E. Geiger, Chem. Rev., 1996, 96, 877-910.

6 M. J. Frisch, et al., Gaussian 16, revision A.03, Wallignford, CT, USA, 2016.

7 C. Adamo, V. Barone, J. Chem. Phys., 1999, 110, 6158-6169.

8 J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev., 2005, 105, 2999-3093.

9 T. Le Bahers, C. Adamo, I. Ciofini, J. Chem. Theory Comput., 2011, 8, 2498-2506.

10 T. Yanai, D. Tew, N. Handy, Chem. Phys. Lett., 2004, 393, 51-57.

11 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Scheleyer, *Chem. Rev.*, 2005, **105**, 3842-3888.