Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Ferrocene analogues of Brooker's Merocyanine: A new library of organometallic inverted solvatochromic dyes

Ignacio Aburto,[a] Fabián Martínez-Gómez,[a] Carolina Aliaga[a,b] and Moisés Domínguez*[a]

[a]Facultad de Química y Biología, Universidad de Santiago de Chile, Av. B.O'Higgins, 3363 Santiago, Chile. E-
[b]Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA, Chile
mail: moises.dominguez@usach.cl

Supplemental material

Contents

1. Characterization data of dye 3–6

1.1 General methods

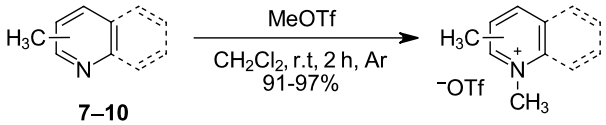
All NMR measurements were recorded on a Bruker Avance NEO 400 spectrometer (Bellerica, MA, USA) operating at 400.13 MHz (^{1}H) and 100.62 MHz (^{13}C). No D-NMR experiments were carried out turning off the lock option. Tuning process was accomplished by automatization, meanwhile shimming was carried out manually, adjusting Z1 to Z4 until finding the maximum area for the signals. For the fine adjustment, X, Y, XY and YZ were used. All experiments were carried out using 32 scans (ns), 4 dummy scans (ds) and a 64K time domain (TD). IR spectra were recorded with a Spectrum Two FT-IR (ATR) Perkin Elmer spectrophotometer HRMS was performed with Varian Ionspec QFT-7 (ESI-FT ICRMS) and Agilent 6210 ESI-TOF instruments. Melting points were recorded with a Microthermal capillary melting-point apparatus and were not corrected. All reagents were reagent grade and were used without further purification. TLC was performed on TLC plates (silica gel 60, fluorescence indicator F254, 0.25 mm layer thickness). Products were purified by recrystallization from ethanol.

UV–Vis spectra were recorded on a diode array UV–vis near IR Specord S 600 (Maximum recording speed for complete spectra: 12 msec) at a room temperature of 23 ± 1 °C. The molar concentration of the dyes in the solutions employed during UV– vis measurements were *ca.* 3×10^{-5} mol/L.

1.2 Synthetic procedures

***N*-methylation of azaheterocycles with methyl triflate; General procedure 1.**

MeOTf (1.5 mmol) was added dropwise to a stirred solution of the corresponding pyridine derivative (1.0 mmol) in dry dichloromethane (5.0 mL) under an argon atmosphere at room temperature. The resulting mixture was stirred during 2 h. After this time, the solid product was filtered off and dried under vacuum.



7–10 **11–14**

1,4-Dimethylpyridium triflate 11. Colorless solid, 91% yield (234 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.67 (d, J = 6.6 Hz, 2H), 7.81 (d, J = 6.2 Hz, 2H), 4.14 (s, 3H), 2.47 (s, 3H) ppm. The analytical data match those reported in the literature.[1]

1,4-Dimethylquinolinium triflate 13. Colorless solid, 94% yield (289 mg), mp. 113-115 °C (lit.[4] 114.6 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.30 – 9.19 (m, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 8.9 Hz, 1H), 8.23 – 8.15 (m, 1H), 8.02 – 7.93 (m, 2H), 4.50 (s, 3H), 2.93 (s, 3H) ppm. The analytical data match those reported in the literature.[4]

1,2-Dimethylpyridinium triflate 12. Colorless solid, 93% yield (239 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.91 – 8.86 (m, 1H), 8.44 – 8.35 (m, 1H), 8.02 – 7.95 (m, 1H), 7.92 – 7.83 (m, 1H), 4.17 (s, 3H), 2.73 (s, 3H) ppm. The analytical data match those reported in the literature.[2,3]

1,2-Dimethylquinolinium 14. Colorless solid, 97% yield (298 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.02 (d, J = 8.6 Hz, 1H), 8.58 – 8.48 (m, 1H), 8.38 – 8.30 (m, 1H), 8.22 – 8.12 (m, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.96 – 7.88 (m, 1H), 4.38 (s, 3H), 3.01 (s, 3H) ppm. The analytical data match those reported in the literature.[5]

Condensation reactions with ferrocencarboxaldehyde; General procedure 2.
Under argon atmosphere, a mixture of the pyridinium salt (1.0 mmol), ferrocencarboxaldehyde (1.5 mmol) and a catalytic amount piperidine (1.0 μL) in dry and degassed ethanol (5 mL) was refluxed at 80 °C for 6 hours. After completion of the reaction as was notice by TLC (EtOAc), the reaction mixture was cooled down to 0 °C overnight. The desired products **3**–**6** were obtained as deeply colored solids after vacuum filtration.

(*E*)-1-methyl-4-[2-(ferrocene-2-yl)ethenyl]pyridinium triflate 3. Purple solid, 70% yield (340 mg), mp. 217-218 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: δ 8.73 (d, J = 6.6 Hz, 2H), 8.06 (d, J = 6.5 Hz, 2H), 7.88 (d, J = 16.0 Hz, 1H), 6.97 (d, J = 16.0 Hz, 1H), 5.04 – 4.65 (m, 2H), 4.65 – 4.48 (m, 2H), 4.23 (s, 5H), 4.18 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ: 153.0, 145.2, 143.6, 122.9, 120.3, 80.5, 72.0, 70.2, 69.2, 47.0 ppm. ^{19}F NMR (376 MHz, DMSO-d_6) δ: -78.99 ppm. FT-IR (ATR) ν: 3055, 1604, 1518, 1253, 1138, 981, 820, 633 cm^{-1}. HRMS (ESI-TOF): m/z [M + H$^+$] calcd for $C_{20}H_{26}FeN^+$: 336.1407; found: 336.1418.

(*E*)-1-methyl-4-[2-(ferrocene-2-yl)ethenyl]quinolinium triflate 4. Purple solid, 78% yield (535 mg), mp. 225-226 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.36 – 9.09 (m, 1H), 9.05 – 8.80 (m, 1H), 8.46 – 8.36 (m, 2H), 8.32 – 7.95 (m, 3H), 7.84 (d, J = 15.6 Hz, 1H), 5.19 – 4.95 (m, 2H), 4.86 – 4.61 (m, 2H), 4.46 (s, 3H), 4.27 (s, 5H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ: 152.7, 147.9, 146.6, 139.4, 135.2, 129.4, 126.7, 126.0, 119.6, 116.6, 115.2, 81.0, 72.6, 70.4, 70.0, 44.8 ppm. ^{19}F NMR (376 MHz, DMSO-d_6) δ: -78.99 ppm. FT-IR (ATR) ν: 3062, 1587, 1560, 1255, 1160, 1024, 759, 632 cm^{-1}. HRMS (ESI-TOF): m/z [M + H$^+$] calcd for $C_{24}H_{28}FeN^+$: 386.1562; found: 386.1571.

(*E*)-1-methyl-2-[2-(ferrocene-2-yl)ethenyl]pyridinium triflate 5. Purple solid, 30% yield (146 mg), mp. 185-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.78 (d, J = 6.3 Hz, 1H), 8.52 – 8.31 (m, 2H), 7.90 – 7.71 (m, 2H), 7.07 (d, J = 15.5 Hz, 1H), 4.90 – 4.84 (m, 2H), 4.68 – 4.60 (m, 2H), 4.27 (s, 5H), 4.25 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ: 153.0, 145.99, 145.96, 144.1, 124.6, 124.1, 113.9, 80.1, 72.2, 70.3, 69.6, 46.2 ppm. ^{19}F NMR (376 MHz, DMSO-d_6) δ: -78.99 ppm. FT-IR (ATR) ν: 3097, 1607, 1564, 1445, 1260, 1174, 1028, 771, 634 cm^{-1}. HRMS (ESI-TOF): m/z [M + H$^+$] calcd for $C_{20}H_{26}FeN^+$: 336.1407; found: 336.1411.

(*E*)-1-methyl-2-[2-(ferrocene-2-yl)ethenyl]quinolinium triflate 6. Purple solid, 37% yield (198 mg), mp. 160-161 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.93 (d, J = 8.9 Hz, 1H), 8.59 – 8.42 (m, 2H), 8.30 (d, J = 7.9 Hz, 1H), 8.23 (d, J = 15.4 Hz, 1H), 8.18 – 8.06 (m, 1H), 7.99 – 7.81 (m, 1H), 7.40 (d, J = 15.4 Hz, 1H), 5.08 – 4.98 (m, 2H), 4.80 – 4.74 (m, 2H), 4.42 (s, 3H), 4.32 (s, 5H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ: 156.2, 151.6, 143.3, 139.6, 135.0, 130.4, 128.9, 127.6, 121.1, 119.5, 115.5, 80.1, 73.4, 70.7, 70.4, 69.9, 66.8 ppm. ^{19}F NMR (376 MHz, DMSO-d_6) δ: -78.99 ppm. FT-IR (ATR) ν: 3093, 1590, 1520, 1453, 1254, 1151, 1026, 820, 634 cm^{-1}. HRMS (ESI-TOF): m/z [M + H$^+$] calcd for $C_{24}H_{28}FeN^+$: 386.1562; found: 386.1568.

1.3 Computational details
The molecular structures of **3**–**6** were optimized at the Becke-Lee-Yang-Parr B3LYP density-functional level of theory (DFT)[6,7] employing the triple-ξ Karlsruhe basis set (def2-TZVP).[8] Dispersion forces were accounted for with Grimme's D3 correction.[9] Frequencies were calculated for all molecules in order to ensure energy minima. The electronic transition energy were calculated over the optimized structures with the TDDFT method at the Becke-Lee-Yang-Parr B3LYP level of theory employing the quadruple-ξ Karlsruhe basis set (def2-TZVP).[8] The solvent effect for dichloromethane solution was included by employing the implicit CPCM solvation model.[10,11] The RI[12,13] and the Chain of Spheres[14] approximations were employed to speed up the optimization and spectrum calculation respectively. All the calculations were carried out in ORCA 5.0.3.[15]

2. Solvatochromic plots E_T *vs.* E_T^N

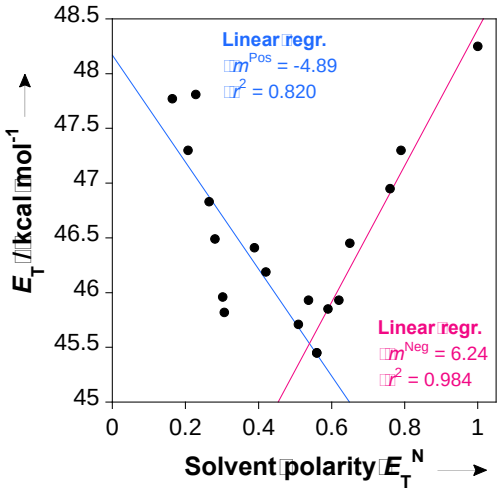


Fig. S1 Variations in the electronic transition energy E_T of dye **4** as a function of normalized solvent polarity values E_T^N and the linear regression of the positive (blue) and negative (pink) parts of its general solvatochromic inverted profile.

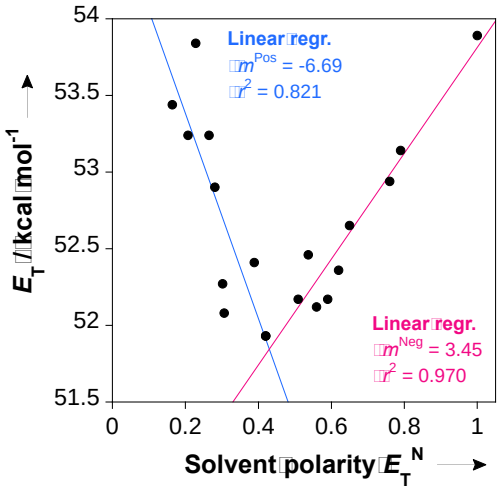


Fig. S2 Variations in the electronic transition energy E_T of dye **5** as a function of normalized solvent polarity values E_T^N and the linear regression of the positive (blue) and negative (pink) parts of its general solvatochromic inverted profile.

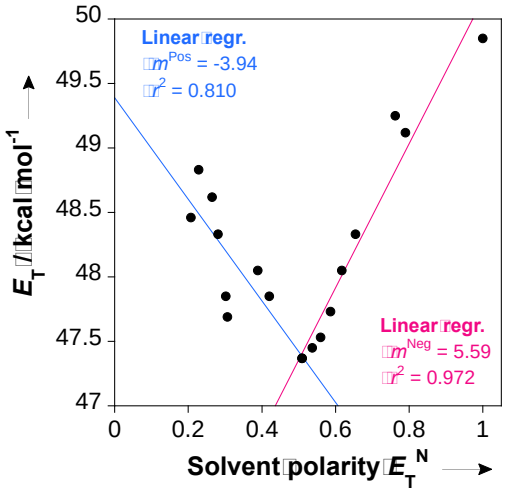


Fig. S3 Variations in the electronic transition energy E_T of dye **6** as a function of normalized solvent polarity values E_T^N and the linear regression of the positive (blue) and negative (pink) parts of its general solvatochromic inverted profile.

Table S1. Linear regressions obtained for dyes **3**–**6**, and polarity at where solvatochromic inversion takes place.

Dye	Equations		E_T^N inversion
	Positive solvatochromism	Negative solvatochromism	
3	$E_T = 55.09 - 13.83\ E_T^N$	$E_T = 49.46 + 2.77\ E_T^N$	0.339
4	$E_T = 48.17 - 4.89\ E_T^N$	$E_T = 42.17 + 6.24\ E_T^N$	0.539
5	$E_T = 54.72 - 6.69\ E_T^N$	$E_T = 50.36 + 3.45\ E_T^N$	0.430
6	$E_T = 49.39 - 3.94\ E_T^N$	$E_T = 44.56 + 5.59\ E_T^N$	0.507

3. Catalán's equations obtained for the solvatochromism of dyes 3–6

Table S2. Catalán's equations obtained for the positive and negative solvatochromic part of the general inverted solvatochromic curve of dyes **3**–**6**.

Dye	Equations			
	Positive solvatochromism		**Negative solvatochromism**	
3	$E_T = 59.17 - 8.04\,SP - 2.28\,SdP$	$r^2 = 0.972$	$E_T = 50.24 + 1.91\,SA$	$r^2 = 0.984$
4	$E_T = 55.38 - 3.34\,SB - 9.11\,SP$	$r^2 = 0.861$	$E_T = 41.90 + 5.92\,SdP$	$r^2 = 0.951$
5	$E_T = 61.77 - 3.24\,SB - 9.57\,SP$	$r^2 = 0.919$	$E_T = 51.66 + 2.08\,SA$	$r^2 = 0.975$
6	$E_T = 53.71 - 2.00\,SB - 5.83\,SP$	$r^2 = 0.947$	$E_T = 44.95 + 4.60\,SdP$	$r^2 = 0.960$

4. Copies of the ^{1}H and ^{13}C NMR spectra of dyes 3–6

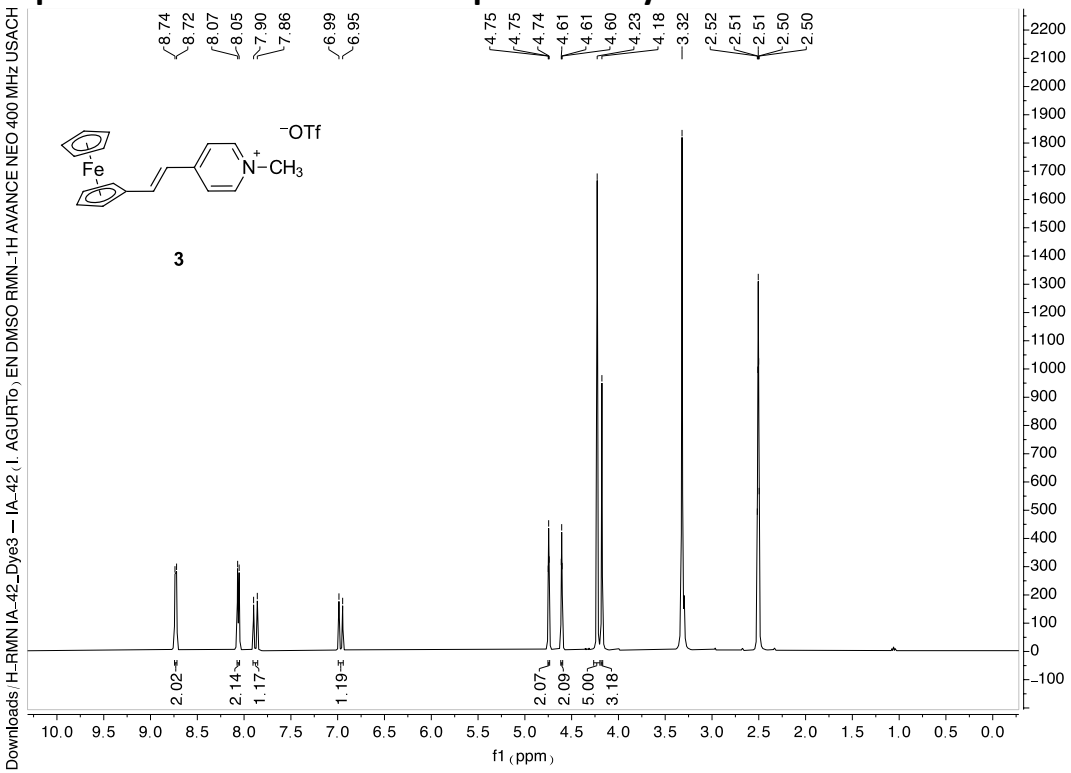


Fig. S4 ^{1}H NMR spectrum of dye **3** recorded in DMSO-d_6.

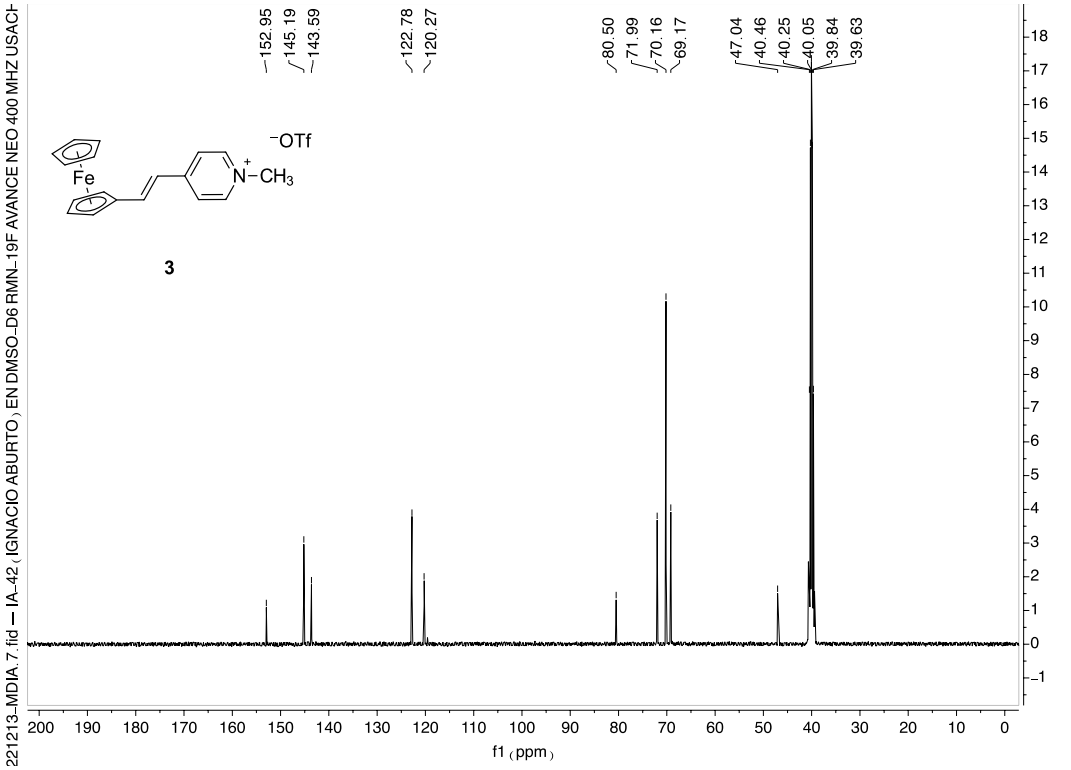


Fig. S5 ^{13}C NMR spectrum of dye **3** recorded in DMSO-d_6.

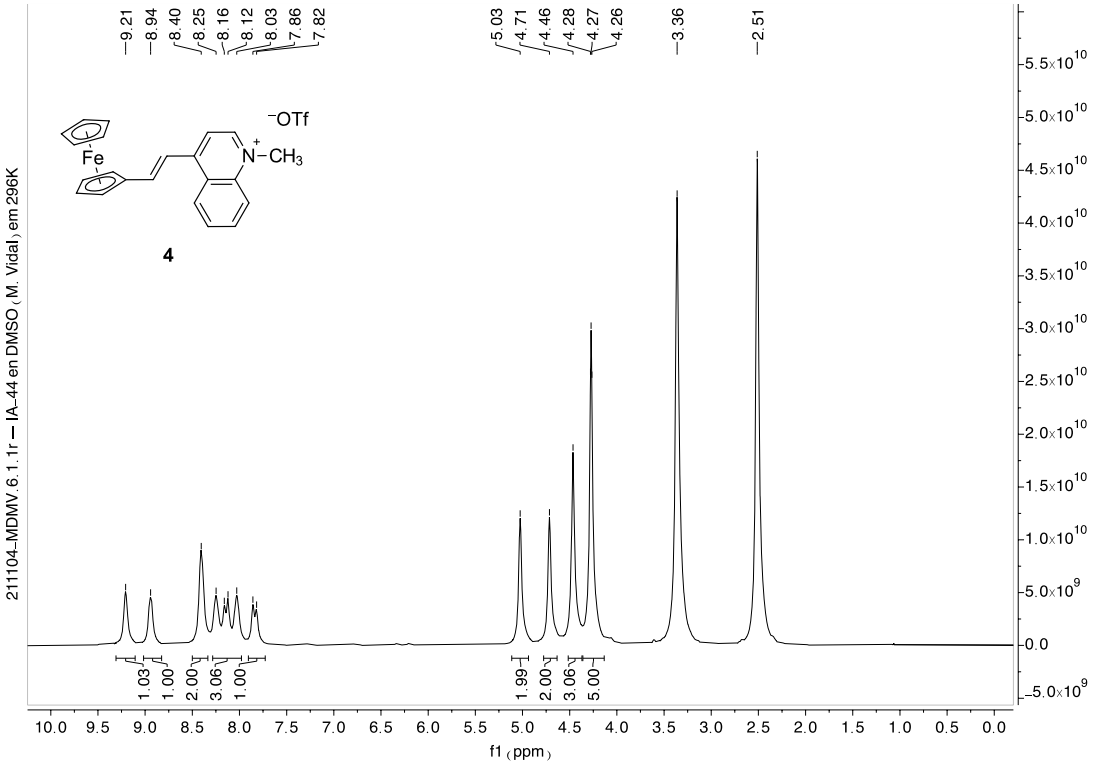


Fig. S6 ^{1}H NMR spectrum of dye **4** recorded in DMSO-d_6.

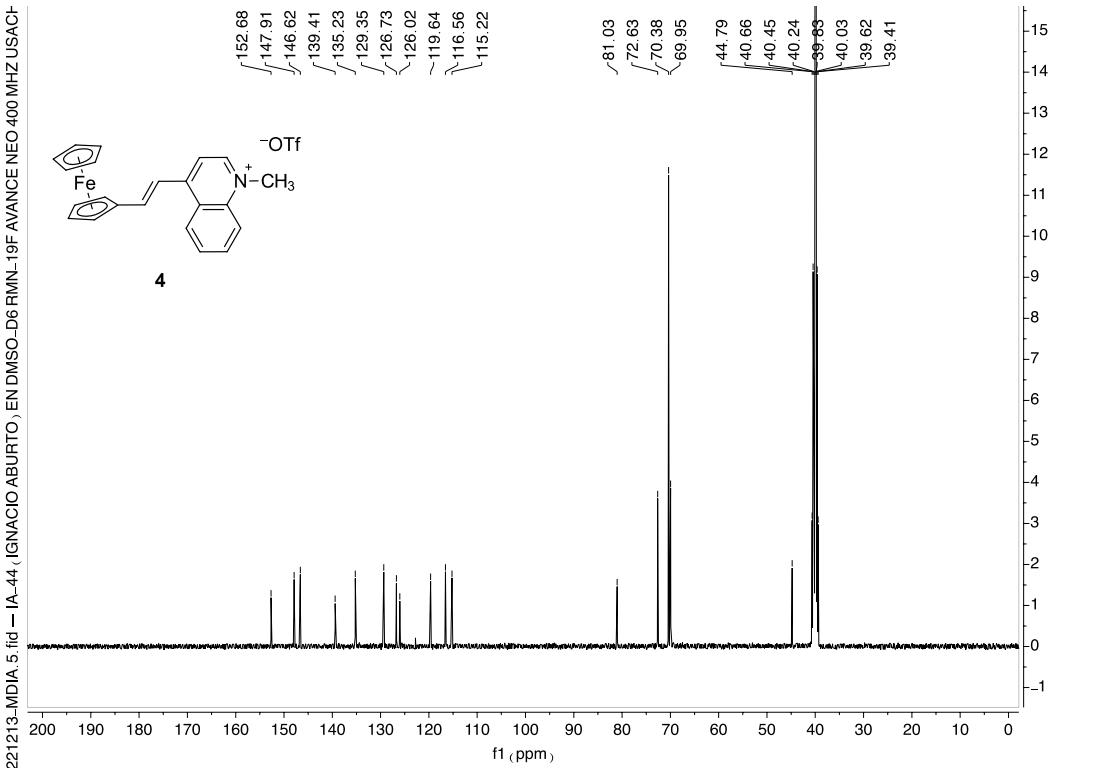


Fig. S7 ^{13}C NMR spectrum of dye **4** recorded in DMSO-d_6.

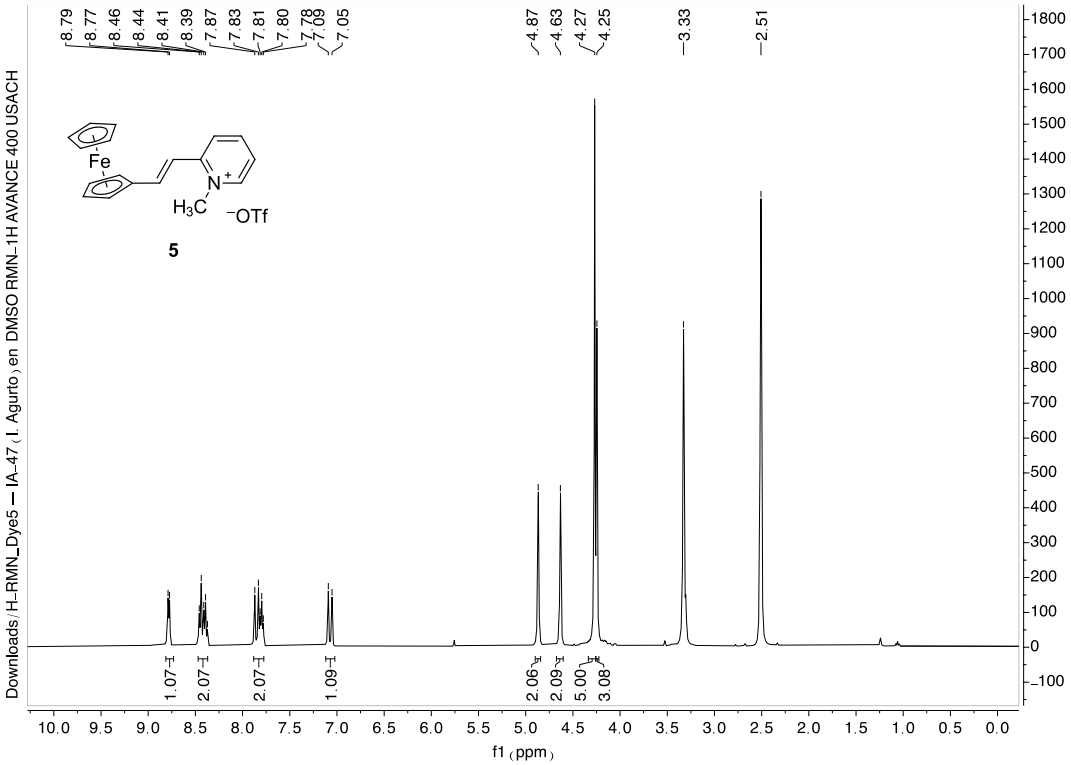


Fig. S8 ^{1}H NMR spectrum of dye **5** recorded in DMSO-d_6.

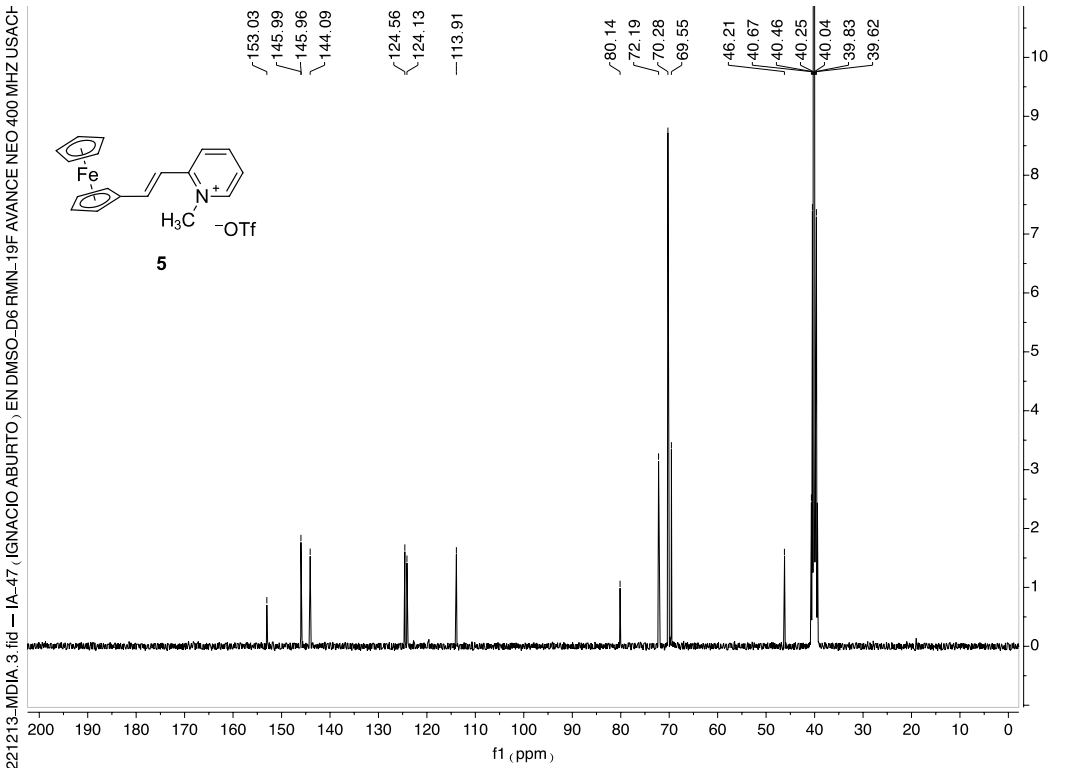


Fig. S9 ^{13}C NMR spectrum of dye **5** recorded in DMSO-d_6.

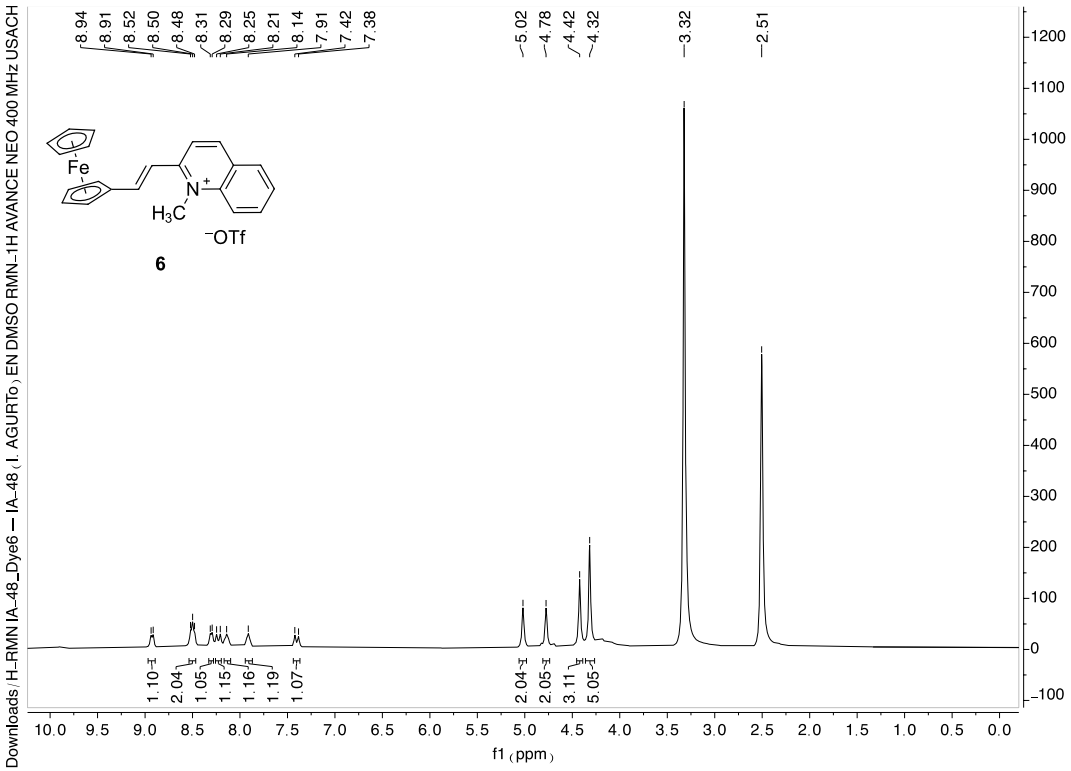


Fig. S10 ^{1}H NMR spectrum of dye **6** recorded in DMSO-d_6.

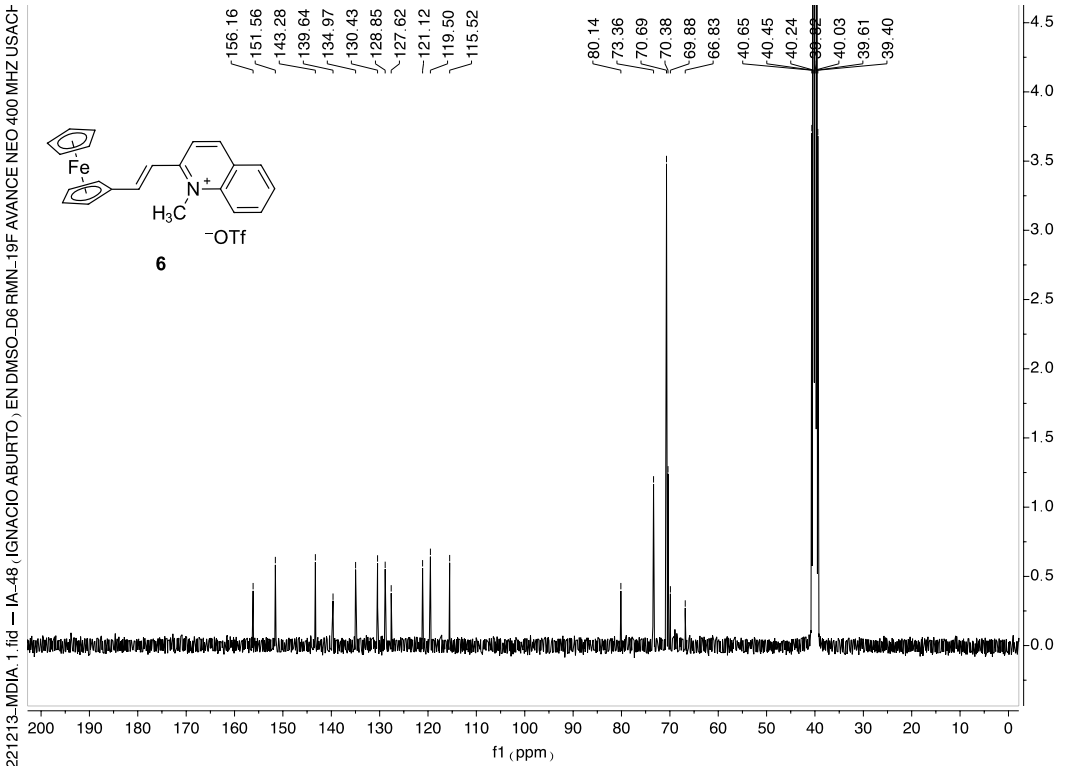


Fig. S11 ^{13}C NMR spectrum of dye **6** recorded in DMSO-d_6.

5. NMR Studies at different temperatures for dye 3

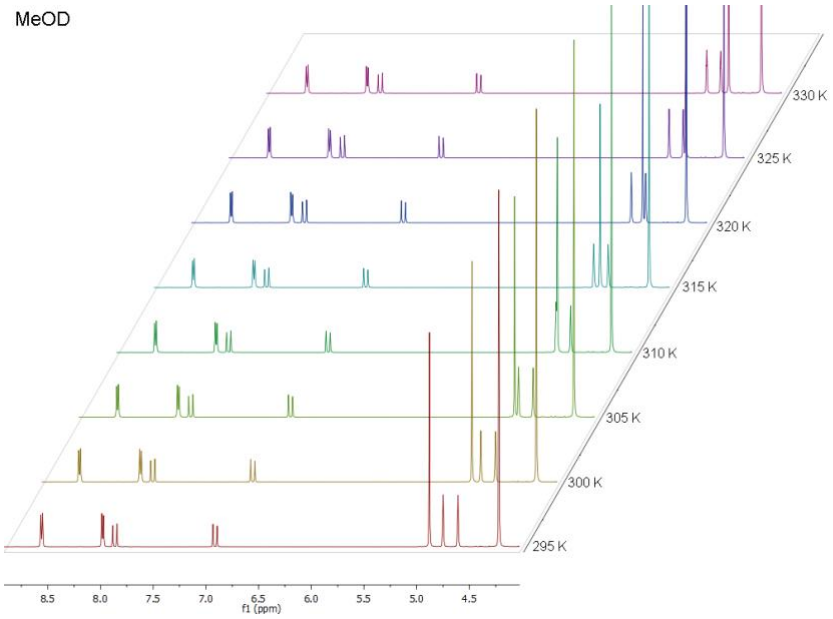


Fig. S12 Variation of the ^{1}H NMR signals of dye **3** in CD_3OD solution at different temperatures.

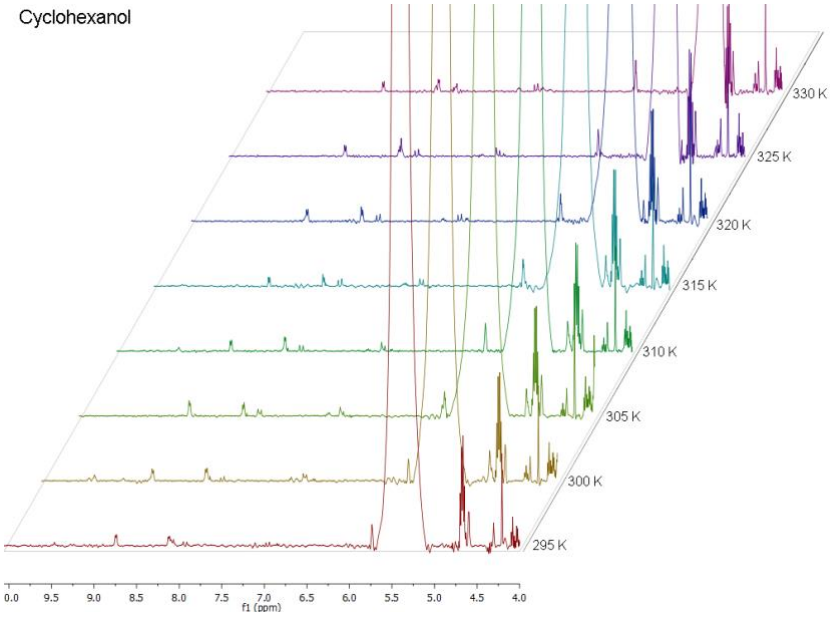


Fig. S13 Variation of the No-D ^{1}H NMR signals of dye **3** in cyclohexanol solution at different temperatures.

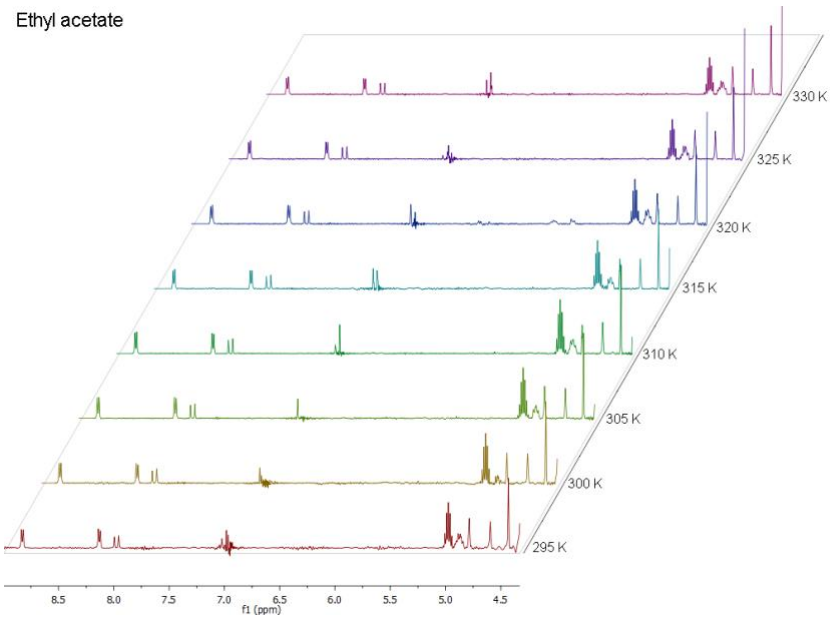


Fig. S14 Variation of the No-D ^{1}H NMR signals of dye **3** in ethyl acetate solution at different temperatures.

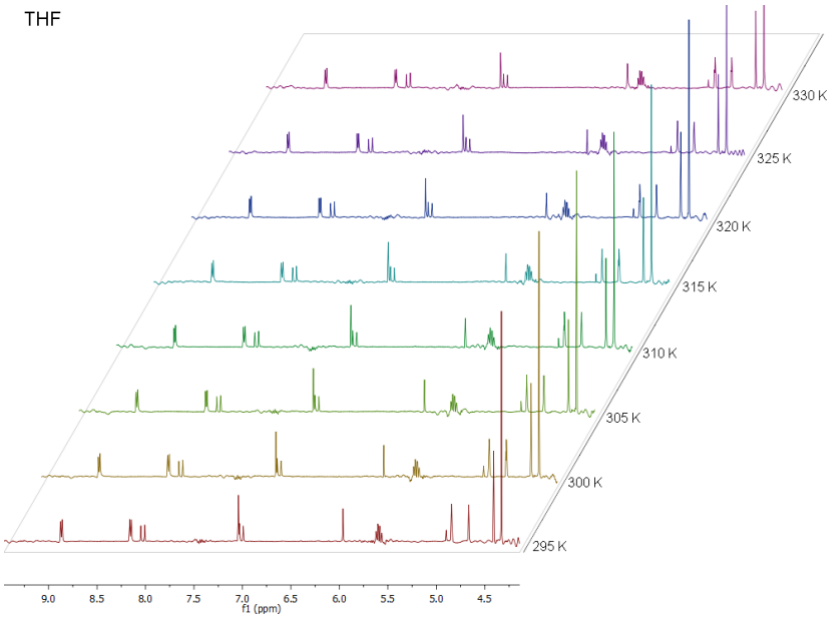


Fig. S15 Variation of the No-D ^{1}H NMR signals of dye **3** in tetrahydrofuran solution at different temperatures.

Table S3. Coupling constant in Hz of the ethylene bridge hydrogens of dye **3** at different temperatures in Kelvin.

Temperature	D_2O	CD_3OD	No-D CyOH	No-D EtOAc	No-D THF
295	16.00	15.95	15.92	16.10	15.98
300	16.01	15.92	15.69	15.91	15.97
305	16.03	15.93	15.63	16.02	15.85
310	15.98	15.91	15.94	16.04	16.00
315	15.98	15.94	16.09	16.07	15.96
320	15.98	15.94	15.67	16.05	16.00
325	15.99	15.91	16.06	15.95	16.00
330	16.02	15.91	16.86	16.05	15.98
335	15.96	–	–	–	–
340	15.97	–	–	–	–

6. EPR spectra of dyes 3–6 in water solution.

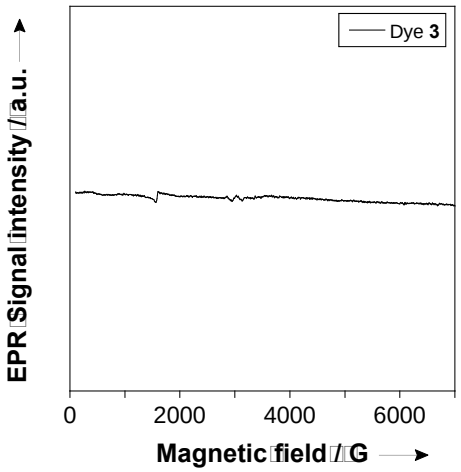


Fig. S16 EPR spectra of dye **3** in water solution.

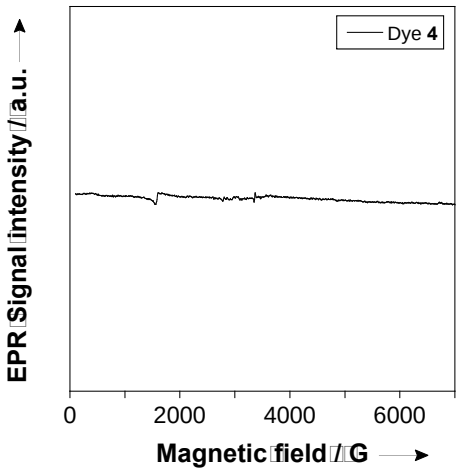


Fig. S17 EPR spectra of dye **4** in water solution.

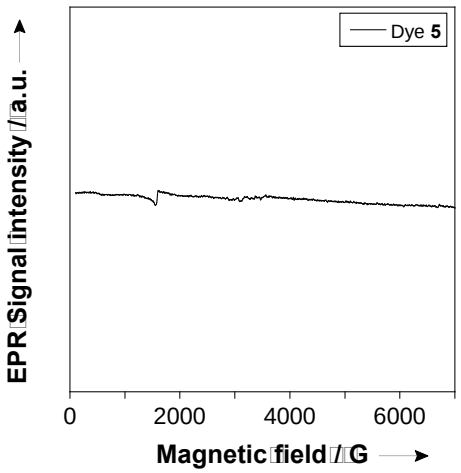


Fig. S18 EPR spectra of dye **5** in water solution.

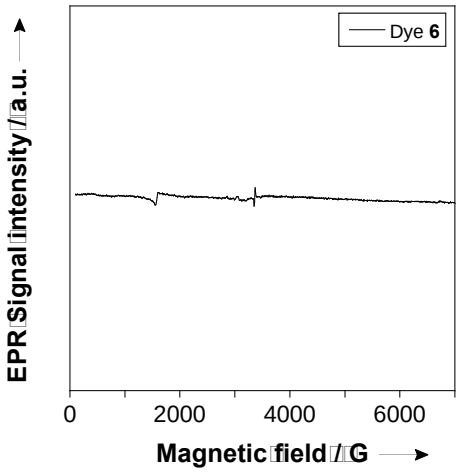


Fig. S19 EPR spectra of dye **6** in water solution.

7. Frontier molecular orbitals of dyes 5 and 6 in water solution

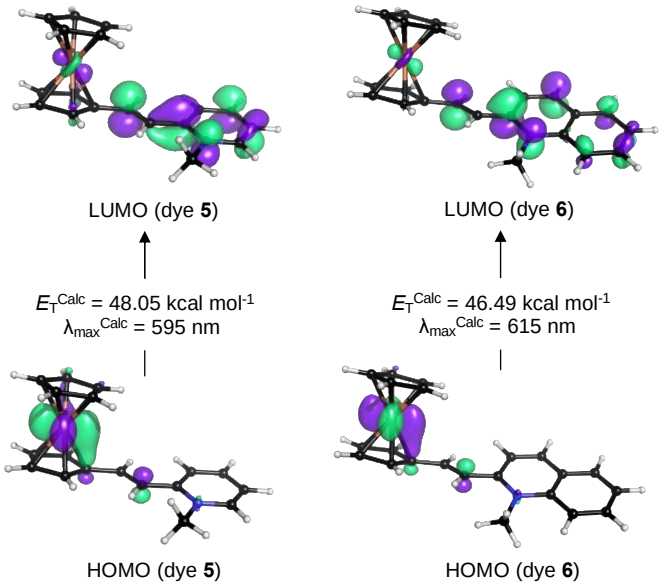


Fig. S20 Frontier molecular orbitals of dyes **5** and **6** in dichloromethane solution, obtained by the TDDFT B3LYP/def2-TZVP CPCM=water method.

8. Dihedral angles of the optimized dyes 3-6 water solution

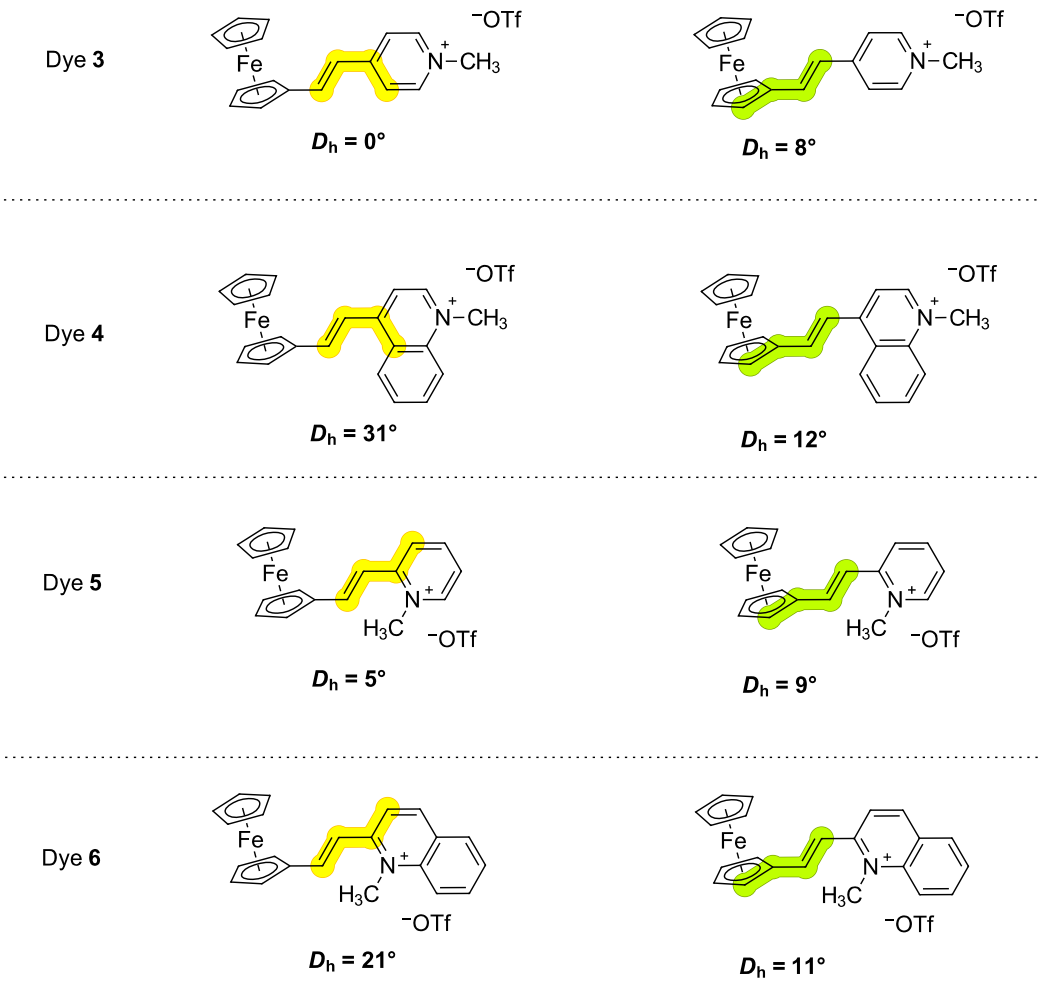


Fig. S21 Dihedral angles of the optimized structures of dyes **3**–**6** in water solution, obtained at the B3LYP/def2-TZVP CPCM=water level of theory.

9. Absorbance measurements of dye 3–6

Table S4. Absorbance of dye **3** in protic solvents at various concentrations.

Solvent	[Dye 3] / mol L^{-1}	Absorbance	λ_{max} / nm
Water	2.49×10^{-5}	0.131	544
	4.13×10^{-5}	0.211	545
	5.77×10^{-5}	0.290	545
	7.39×10^{-5}	0.379	544
	9.00×10^{-5}	0.462	545
	1.06×10^{-4}	0.548	545
	1.22×10^{-4}	0.620	544
1,2-Ethanediol	2.49×10^{-5}	0.089	552
	4.13×10^{-5}	0.163	552
	5.77×10^{-5}	0.260	553
	7.39×10^{-5}	0.345	554
	9.00×10^{-5}	0.480	552
	1.06×10^{-4}	0.531	552
	1.22×10^{-4}	0.615	552
Methanol	2.49×10^{-5}	0.142	553
	4.13×10^{-5}	0.235	554
	5.77×10^{-5}	0.326	554
	7.39×10^{-5}	0.418	554
	9.00×10^{-5}	0.514	554
	1.06×10^{-4}	0.607	554
	1.22×10^{-4}	0.696	555
Ethanol	2.49×10^{-5}	0.149	558
	4.13×10^{-5}	0.246	558
	5.77×10^{-5}	0.346	558
	7.39×10^{-5}	0.440	557
	9.00×10^{-5}	0.538	558
	1.06×10^{-4}	0.633	558
	1.22×10^{-4}	0.728	557
1-Propanol	2.49×10^{-5}	0.149	562
	4.13×10^{-5}	0.248	562
	5.77×10^{-5}	0.348	562
	7.39×10^{-5}	0.449	562
	9.00×10^{-5}	0.552	560
	1.06×10^{-4}	0.657	562
	1.22×10^{-4}	0.756	562
1-Butanol	2.49×10^{-5}	0.146	564
	4.13×10^{-5}	0.247	565
	5.77×10^{-5}	0.350	564
	7.39×10^{-5}	0.451	565
	9.00×10^{-5}	0.546	564
	1.06×10^{-4}	0.646	564
	1.22×10^{-4}	0.751	562
1-Hexanol	2.49×10^{-5}	0.153	563
	4.13×10^{-5}	0.258	563
	5.77×10^{-5}	0.350	563

	7.39×10^{-5}	0.452	562
	9.00×10^{-5}	0.552	563
	1.06×10^{-4}	0.652	563
	1.22×10^{-4}	0.746	562
1-Octanol	2.49×10^{-5}	0.158	559
	4.13×10^{-5}	0.244	560
	5.77×10^{-5}	0.337	558
	7.39×10^{-5}	0.436	558
	9.00×10^{-5}	0.534	556
	1.06×10^{-4}	0.630	559
	1.22×10^{-4}	0.728	557
1-Cyclohexanol	2.49×10^{-5}	0.173	563
	4.13×10^{-5}	0.275	562
	5.77×10^{-5}	0.375	562
	7.39×10^{-5}	0.513	562
	9.00×10^{-5}	0.559	560
	1.06×10^{-4}	0.665	562
	1.22×10^{-4}	0.782	564
tert-Butanol	2.49×10^{-5}	0.148	561
	4.13×10^{-5}	0.246	558
	5.77×10^{-5}	0.340	559
	7.39×10^{-5}	0.433	559
	9.00×10^{-5}	0.526	556
	1.06×10^{-4}	0.617	559
	1.22×10^{-4}	0.706	558

Table S5. Absorbance of dye **4** in protic solvents at various concentrations.

Solvent	**[Dye 4] / mol L^{-1}**	**Absorbance**	**λ_{max} / nm**
Water	2.49×10^{-5}	0.161	592
	4.13×10^{-5}	0.275	593
	5.77×10^{-5}	0.389	592
	7.39×10^{-5}	0.521	593
	9.00×10^{-5}	0.627	595
	1.06×10^{-4}	0.740	594
	1.22×10^{-4}	0.836	594
1,2-Ethanediol	2.49×10^{-5}	0.090	603
	4.13×10^{-5}	0.226	603
	5.77×10^{-5}	0.353	603
	7.39×10^{-5}	0.478	603
	9.00×10^{-5}	0.612	603
	1.06×10^{-4}	0.737	604
	1.22×10^{-4}	0.860	602

Methanol	2.49×10^{-5}	0.202	607
	4.13×10^{-5}	0.326	610
	5.77×10^{-5}	0.449	609
	7.39×10^{-5}	0.584	609
	9.00×10^{-5}	0.709	611
	1.06×10^{-4}	0.835	609
	1.22×10^{-4}	0.960	609
Ethanol	2.49×10^{-5}	0.186	616
	4.13×10^{-5}	0.321	614
	5.77×10^{-5}	0.454	612
	7.39×10^{-5}	0.580	614
	9.00×10^{-5}	0.711	615
	1.06×10^{-4}	0.840	615
	1.22×10^{-4}	0.968	612
1-Propanol	2.49×10^{-5}	0.202	621
	4.13×10^{-5}	0.339	624
	5.77×10^{-5}	0.471	623
	7.39×10^{-5}	0.606	622
	9.00×10^{-5}	0.727	620
	1.06×10^{-4}	0.856	621
	1.22×10^{-4}	0.993	621
1-Butanol	2.49×10^{-5}	0.207	623
	4.13×10^{-5}	0.342	625
	5.77×10^{-5}	0.481	625
	7.39×10^{-5}	0.612	625
	9.00×10^{-5}	0.749	625
	1.06×10^{-4}	0.891	622
	1.22×10^{-4}	1.029	621
1-Hexanol	2.49×10^{-5}	0.211	627
	4.13×10^{-5}	0.347	626
	5.77×10^{-5}	0.471	625
	7.39×10^{-5}	0.606	625
	9.00×10^{-5}	0.733	628
	1.06×10^{-4}	0.855	624
	1.22×10^{-4}	0.996	628

Table S5. Absorbance of dye **5** in protic solvents at various concentrations.

Solvent	**[Dye 5] / mol L^{-1}**	**Absorbance**	**λ_{max} / nm**
Water	2.49×10^{-5}	0.098	531
	4.13×10^{-5}	0.164	528
	5.77×10^{-5}	0.234	528
	7.39×10^{-5}	0.298	530
	9.00×10^{-5}	0.358	529
	1.06×10^{-4}	0.424	531
	1.22×10^{-4}	0.488	530

1,2-Ethanediol	2.49×10^{-5}	0.137	537
	4.13×10^{-5}	0.195	537
	5.77×10^{-5}	0.252	537
	7.39×10^{-5}	0.333	537
	9.00×10^{-5}	0.404	539
	1.06×10^{-5}	0.475	537
	1.22×10^{-5}	0.537	537
Methanol	2.49×10^{-5}	0.115	540
	4.13×10^{-5}	0.190	542
	5.77×10^{-5}	0.269	541
	7.39×10^{-5}	0.349	540
	9.00×10^{-5}	0.424	539
	1.06×10^{-4}	0.501	539
	1.22×10^{-4}	0.579	540
Ethanol	2.49×10^{-5}	0.116	540
	4.13×10^{-5}	0.190	540
	5.77×10^{-5}	0.257	542
	7.39×10^{-5}	0.327	542
	9.00×10^{-5}	0.396	542
	1.06×10^{-4}	0.456	542
	1.22×10^{-4}	0.527	542
1-Propanol	2.49×10^{-5}	0.129	546
	4.13×10^{-5}	0.208	546
	5.77×10^{-5}	0.291	546
	7.39×10^{-5}	0.369	546
	9.00×10^{-5}	0.446	546
	1.06×10^{-4}	0.526	545
	1.22×10^{-4}	0.606	546
1-Butanol	2.49×10^{-5}	0.118	547
	4.13×10^{-5}	0.191	547
	5.77×10^{-5}	0.278	547
	7.39×10^{-5}	0.367	548
	9.00×10^{-5}	0.440	548
	1.06×10^{-4}	0.525	547
	1.22×10^{-4}	0.606	547
1-Hexanol	2.49×10^{-5}	0.119	549
	4.13×10^{-5}	0.197	549
	5.77×10^{-5}	0.284	549
	7.39×10^{-5}	0.367	547
	9.00×10^{-5}	0.450	549
	1.06×10^{-5}	0.537	549
	1.22×10^{-4}	0.614	549
1-Octanol	2.49×10^{-5}	0.117	546
	4.13×10^{-5}	0.194	546
	5.77×10^{-5}	0.274	546
	7.39×10^{-5}	0.343	546
	9.00×10^{-5}	0.426	546
	1.06×10^{-4}	0.505	543
	1.22×10^{-4}	0.566	546
1-Cyclohexanol	2.49×10^{-5}	0.109	546

	4.13×10^{-5}	0.208	547
	5.77×10^{-5}	0.298	546
	7.39×10^{-5}	0.400	546
	9.00×10^{-5}	0.506	547
	1.06×10^{-4}	0.575	547
	1.22×10^{-4}	0.672	546

Table S6. Absorbance of dye **6** in protic solvents at various concentrations.

Solvent	**[Dye 6] / mol L^{-1}**	**Absorbance**	**λ_{max} / nm**
Water	2.49×10^{-5}	0.128	570
	4.13×10^{-5}	0.216	574
	5.77×10^{-5}	0.303	571
	7.39×10^{-5}	0.393	574
	9.00×10^{-5}	0.482	572
	1.06×10^{-4}	0.573	573
	1.22×10^{-4}	0.661	573
1,2-Ethanediol	2.49×10^{-5}	0.116	584
	4.13×10^{-5}	0.206	583
	5.77×10^{-5}	0.306	583
	7.39×10^{-5}	0.387	583
	9.00×10^{-5}	0.478	583
	1.06×10^{-4}	0.569	583
	1.22×10^{-4}	0.721	584
Methanol	2.49×10^{-5}	0.135	584
	4.13×10^{-5}	0.235	583
	5.77×10^{-5}	0.331	586
	7.39×10^{-5}	0.420	587
	9.00×10^{-5}	0.519	584
	1.06×10^{-4}	0.610	584
	1.22×10^{-4}	0.696	583
Ethanol	2.49×10^{-5}	0.135	593
	4.13×10^{-5}	0.225	587
	5.77×10^{-5}	0.309	589
	7.39×10^{-5}	0.402	589
	9.00×10^{-5}	0.485	589
	1.06×10^{-4}	0.574	592
	1.22×10^{-4}	0.649	589
1-Propanol	2.49×10^{-5}	0.136	594
	4.13×10^{-5}	0.243	595
	5.77×10^{-5}	0.363	596
	7.39×10^{-5}	0.464	596
	9.00×10^{-5}	0.570	596
	1.06×10^{-4}	0.675	594
	1.22×10^{-4}	0.778	595
1-Butanol	2.49×10^{-5}	0.155	597

	4.13×10^{-5}	0.267	598
	5.77×10^{-5}	0.377	598
	7.39×10^{-5}	0.482	598
	9.00×10^{-5}	0.592	598
	1.06×10^{-4}	0.706	598
	1.22×10^{-4}	0.816	598
1-Hexanol	2.49×10^{-5}	0.173	601
	4.13×10^{-5}	0.276	601
	5.77×10^{-5}	0.388	601
	7.39×10^{-5}	0.495	601
	9.00×10^{-5}	0.598	600
	1.06×10^{-4}	0.714	601
	1.22×10^{-4}	0.827	601
1-Octanol	2.49×10^{-5}	0.157	604
	4.13×10^{-5}	0.256	601
	5.77×10^{-5}	0.365	602
	7.39×10^{-5}	0.493	602
	9.00×10^{-5}	0.589	602
	1.06×10^{-4}	0.703	603
	1.22×10^{-4}	0.797	601
1-Cyclohexanol	2.49×10^{-5}	0.153	603
	4.13×10^{-5}	0.236	602
	5.77×10^{-5}	0.354	603
	7.39×10^{-5}	0.469	602
	9.00×10^{-5}	0.594	602
	1.06×10^{-4}	0.751	602
	1.22×10^{-4}	0.832	599

10. Absorption coefficients of dyes 3–6 in protic solvents

Table S7. Absorption coefficients ε in L mol^{-1} cm^{-1} of dyes **3**–**6** in protic solvents.

Solvent	Dye 3	Dye 4	Dye 5	Dye 6
Water	5103.2	7052.3	4004.7	5497.4
1,2-Ethanediol	5585.0	7928.9	4220.9	5995.0
Methanol	5722.7	7843.1	4782.6	5785.9
Ethanol	5968.1	8037.6	4202.4	5329.1
1-Propanol	6281.8	8088.2	4908.2	6612.2
1-Butanol	6200.2	8461.3	5066.2	6786.3
1-Hexanol	6113.3	8018.6	5151.4	6730.1
1-Octanol	5917.5	–[a]	4679.6	6709.0
Cyclohexanol	6153.7	–[a]	5809.9	7303.6
tert-butanol	5741.4	–[a]	–[a]	–[a]

[a]Not recorded because the dye exhibited positive solvatochromism in this solvent.

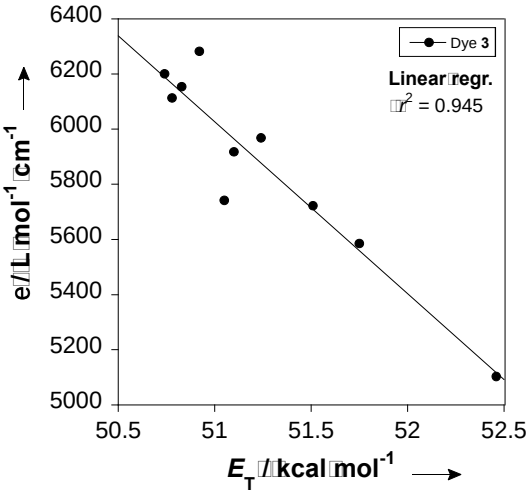


Fig. S22 Correlation of the molar absorption coefficient at the UV/Vis peak maximum, as the function of the electronic transition energy E_T of dye **3** in all the solvents where this dye displays negative solvatochromism.

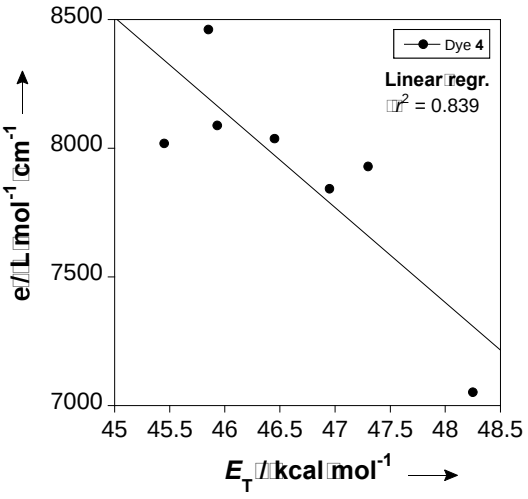


Fig. S23 Correlation of the molar absorption coefficient at the UV/Vis peak maximum, as the function of the electronic transition energy E_T of dye **4** in all the solvents where this dye displays negative solvatochromism.

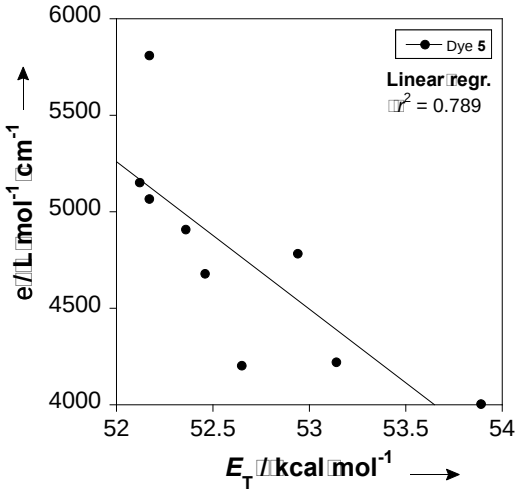


Fig. S24 Correlation of the molar absorption coefficient at the UV/Vis peak maximum, as the function of the electronic transition energy E_T of dye **5** in all the solvents where this dye displays negative solvatochromism.

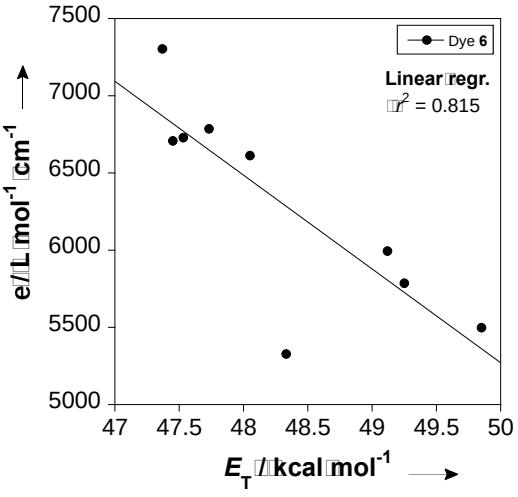


Fig. S25 Correlation of the molar absorption coefficient at the UV/Vis peak maximum, as the function of the electronic transition energy E_T of dye **6** in all the solvents where this dye displays negative solvatochromism.

9. References

1 S. R. Marder, J. W. Perry, B. G. Tiemann and W. P. Schaefer, *Organometallics*, 1991, **10**, 1896–1901.
2 J. A. Cabeza, I. del Río, E. Pérez-Carreño, M. G. Sánchez-Vega and D. Vázquez-García, *Organometallics*, 2010, **29**, 4464–4471.
3 J. A. Bautista-Martinez, L. Tang, J.-P. Belieres, R. Zeller, C. A. Angell and C. Friesen, *J. Phys. Chem. C Nanomater. Interfaces*, 2009, **113**, 12586–12593.
4 A. Motaleb, A. Bera and P. Maity, *Org. Biomol. Chem.*, 2018, **16**, 5081–5085.
5 H. Neelakantan, H.-Y. Wang, V. Vance, J. D. Hommel, S. F. McHardy and S. J. Watowich, *J. Med. Chem.*, 2017, **60**, 5015–5028.
6 A. D. Becke, *Phys. Rev. A Gen. Phys.*, 1988, **38**, 3098–3100.
7 J. P. Perdew, *Phys. Rev. B Condens. Matter*, 1986, **33**, 8822–8824.
8 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
9 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
10 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.
11 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.
12 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **242**, 652–660.
13 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
14 F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98–109.
15 F. Neese, *WIREs Comput Mol Sci*, 2018, **8**, 33.