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Simple dissymmetrical and asymmetrical Tröger's Bases: Photophysical and structural characterization

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Contents

1. Experimental procedures and characterization data

General remarks

All reagents and solvents were purchased from commercial suppliers and used without further purification. All compounds were characterized by ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy using a Bruker Avance II 500 or a Bruker 600 MHz spectrometer. ^{1}H NMR and ^{13}C NMR spectra were supplemented by 2D gradient selected correlation spectroscopy (COSY), multiplicity–edited heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC) and phase sensitive nuclear Overhauser effect spectroscopy (NOESYPH) experiments to help with the assignment of signals. All NMR spectra were processed using the MestReNova software. Chemical shifts (δ) are given in ppm downfield from TMS as the internal standard and coupling constant (J) values are given in Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), multiplet (m), broad singlet (b.s.), doublet of doublets (dd) and complex signal (c.s., mixture of different conformer's peaks that are not possible to integrate separately). ESI–Q–TOF–MS measurements were performed with a Bruker micrOTOF–Q II mass spectrometer running in the positive ion mode at 4.5 kV at a desolvation temperature of 200˚C. Fourier transform infrared spectra were recorded on a FTIR Nicolet 8700 in ATR mode.

General procedure and characterization of compounds 2–3

4,10-dimethyl-2,8-dinitro-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5] diazocine (**3**): 2-methyl-4-nitroaniline (10.0 g, 0.066 mol) was dissolved in trifluoroacetic acid (TFA, 80 ml) previously cooled in an ice bath and paraformaldehyde (4.77g, 0.16 mol) was added in portions. The reaction mixture was allowed to reach ambient temperature and was kept with stirring for 48 h and finally poured into water. The resulting suspension was basified to pH 9 with NaOH 20% and the yellow solid was filtered and resuspended in hot acetone for 20 min. After cooling, the mixture was kept at –20 °C for 16 h and afterwards the solid product was filtered and dried (9.79 g, 0.029 mol, 87 %). The crude product was pure according to NMR spectroscopic analysis.[1]

^{1}H NMR (600 MHz, DMSO–d_6): δ 7.97 (s, 2 H, H–3/9), 7.82 (s, 2 H, H–1/7), 4.68 (d, $J_{endo,exo}$ = 17.3 Hz, 2 H, H–6/12$_{exo}$), 4.37 (s, 2 H, NCH_2N), 4.32 (d, $J_{endo,exo}$ = 17.3 Hz, 2 H, H–6/12$_{endo}$), 2.48 (s, 6 H, CH_3). ^{13}C NMR (150 MHz, DMSO–d_6): δ 152.5 (C–4A/10A), 143.2 (C–2/8), 135.0 (C–4/10), 129.8 (C–1A/7A),

123.9 (C–1/7), 120.8 (C–3/9), 66.6 (NCH_2N), 54.5 (C–6/12), 17.3 (CH_3). HRMS (ESI): m/z calcd. for $C_{17}H_{17}N_4O_4^+$: 341.1244 [*M*+H]$^+$; found 341.1259.

4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine-2,8-diamine (**2a**): Dinitro–TB **3** (1.44 g, 4.2 mmol) and iron powder (4.76 g, 85.3 mmol) were suspended in ethanol (50 ml) and acetic acid (7.0 ml, 122.5 mmol) was added. The mixture was refluxed for 18 h under nitrogen atmosphere, was poured into water and the excess iron powder was filtered. The aqueous solution was extracted with dichloromethane and the organic phase was washed with sat. aq. $NaHCO_3$ and water, dried over Na_2SO_4 and evaporated to dryness. A white solid was obtained, which was pure according to NMR spectroscopic analysis (1.18 g, 4.2 mmol, 99 %).[1]

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.41 (d, $J_{1,3/7,9}$ = 2.0 Hz, 2 H, H–3/9), 6.09 (d, $J_{1,3/7,9}$ = 2.0 Hz, 2 H, H–1/7), 4.45 (d, $J_{endo,exo}$ = 16.7 Hz, 2 H, H–6/12$_{exo}$), 4.27 (s, 2 H, NCH_2N), 3.80 (d, $J_{endo,exo}$ = 16.7 Hz, 2 H, H–6/12$_{endo}$), 3.37 (b.s., 4 H, NH_2), 2.31 (s, 6 H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.3 (C–2/8), 137.7 (C–4A/10A), 133.8 (C–4/10), 129.0 (C–1A/7A), 116.3 (C–3/9), 110.4 (C–1/7), 68.1 (NCH_2N), 55.4 (C–6/12), 17.0 (CH_3). IR (neat): ν̃ = 3417 (w), 3318 (w), 3203 (w) cm^{-1} (NH). HRMS (ESI): m/z calcd. for $C_{17}H_{21}N_4^+$: 281.1761 [*M*+H]$^+$; found 281.1759.

8-isocyano-4,10-dimethyl-6H,12H-5,11-ethanodibenzo[b,f][1,5] diazocin-2-amine (**2b**): Diamino–TB **2a** (0.20 g, 0.71 mmol) was suspended in chloroform/ethanol 3:1 (1.3 ml) and a solution of potassium hydroxide (0.44 g, 7.9 mmol) in water (2.0 ml) was slowly added. The suspension was refluxed for 6 h and afterwards the reaction mixture was diluted with dichloromethane, washed with water, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified using column chromatography on aluminium oxide (CH_2Cl_2 : petroleum ether). A white solid was obtained, which was pure according to NMR spectroscopic analysis (8 mg, 0.03 mmol, 4 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (s, 1 H, H–9), 6.82 (s, 1 H, H–7), 6.45 (d, 1 H, $J_{1,3}$ = 2.3 Hz, H–3), 6.10 (d, 1 H, $J_{1,3}$ = 2.3 Hz, H–1), 4.51 (d, 1 H, $J_{endo,exo}$ = 16.5 Hz, H–12$_{exo}$), 4.49 (d, 1 H, $J_{endo,exo}$ = 17.0 Hz, H–6$_{exo}$), 4.30 (dd, 1 H, $J_{A,B}$ = 12.6 Hz, $J_{B,6–endo}$ = 1,7 Hz, H–NCH$_{A}$H$_{B}$N), 4.23 (dd, 1 H, $J_{A,B}$ = 12.6 Hz, $J_{A,12–endo}$ = 1,5 Hz, H–NCH$_{A}$H$_{B}$N), 3.89 (dd, 1 H, $J_{endo,exo}$ = 17.0 Hz, $J_{B,6–endo}$ = 1.7 Hz, H–6$_{endo}$), 3.84 (dd, 1 H, $J_{endo,exo}$ = 16.5 Hz, $J_{A,12–endo}$ = 1,5 Hz, H–12$_{endo}$), 3.42 (b.s., 2 H, NH_2), 2.38 (s, 3 H, $C_{10}CH_3$), 2.32 (s, 3 H, C_4CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5 (CN), 147.5 (C–10A), 142.6 (C–2), 136.9 (C–4A), 134.5 (C–10), 134.1 (C–4), 129.7 (C–7A), 128.2 (C–1A), 126.5 (C–9), 122.5 (C–7), 121.7 (C–8), 116.6 (C–3), 110.0 (C–1), 67.6 (NCH_2N), 55.1 (C–6), 55.0 (C–12), 17.0 (C_4CH_3), 16.9 ($C_{10}CH_3$). IR (neat): ν̃ = 3438

(w), 3348 (w), 3226 (w) cm^{-1} (NH); 2125 (m) cm^{-1} (NC). HRMS (ESI): m/z calcd. for $C_{18}H_{19}N_4^+$: 291.3775 [*M*+H]$^+$; found 291.1616.

N,N'-(4,10-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-diyl)diformamide (**2d**): Acetic formic anhydride was obtained by stirring a mixture of formic acid (1.3 mL, 35 mmol) and acetic anhydride (2.2 mL, 23 mmol) at 60 °C for 3 h. This mixture was added dropwise to a solution of diamino–TB **2a** (0,26 g, 0.92 mmol) and triethylamine (1,0 mL) in 10 mL of THF, and the reaction mixture was stirred at room temperature for 24 h. The solution was diluted with ethyl acetate (50 mL), washed successively with sat. aq. $KHCO_3$, brine and water, dried over Na_2SO_4 and then concentrated under reduced pressure to give a yellow solid (0.30g, 0.89 mmol, 96 %). The crude product was pure according to NMR spectroscopic analysis. Further purification using column chromatography on silica gel (CH_2Cl_2 : MeOH) afforded a white solid.[1]

^{1}H NMR (500 MHz, CDCl3) δ 8,52–8,47 (c.s., 1 H, CHO, *E*), 8,29 (s, 1 H, CHO, *Z*), 8,02–7,92 (c.s., 1 H, NH, *E*), 7,17–7,13 (m, 1 H, H–1/7, *Z*), 7,06–7,02 (m, 1 H, H–3/9, *Z*), 7,01 (b.s., 1 H, NH, *Z*), 6,81–6,76 (c.s., 1 H, H–3/9, *E*), 6,52–6,47 (m, 1 H, H–1/7, *E*), 4,58–4,50 (c.s., 2 H, H–6/12$_{exo}$), 4,28 (s, 2 H, NCH_2N), 3,97–3,89 (c.s., 2 H, H–6/12$_{endo}$), 2,41–2,36 (c.s., 6 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162,8 / 162,7 (CHO, *E*), 158,7 / 158,7 (CHO, *Z*), 143,6 / 143,4 (C–4A/10A, *E*), 142,8 / 142,7 (C–4A/10A, *Z*), 134,9 / 134,9 (C–4/10, *E*), 133,9 / 133,92 (C–4/10, Z), 132,5 / 132,4 / 132,2 / 132,1 (C–1A/7A, *E* / *Z*), 129,4 / 129,3 (C–2/8, *Z*), 128,7 / 128,6 (C–2/8, *E*), 120,8 / 120,7 (C–3/9, *Z*), 120,3 / 120,2 (C–3/9, *E*), 116,2 / 116,1 (C–1/7, *Z*), 115,1 / 115,0 (C–1/7, *E*), 67,6 / 67,6 / 67,5 (NCH_2N, *E* / *Z*), 55,2 (C–6/12, *Z*), 55,1 (C–6/12, *E*), 17,1 / 17,1 (CH_3, *E* / *Z*). Approx. *Z* / *E* overall ratio: 50:50. IR (neat): ṽ = 3298 (w) (NH); 1660 (s) cm^{-1} (CO). HRMS (ESI): m/z calcd. for $C_{19}H_{21}N_4O_2^+$: 337.1659 [*M*+H]$^+$; found 337.1670.

2,8-Diisocyano-4,10-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5] diazocine (**2c**): Diformamido–TB **2d** (63 mg, 0.19 mmol) and triethylamine (0.25 ml) were dissolved in dichloromethane (5 ml) and phosphorus oxychloride (0.05 ml, 0.53 mmol) in 1 ml dichloromethane was added slowly in an ice bath. After 15 min at 0°C no reacting material was observed by TLC, and the reaction mixture was diluted with 100 ml cyclohexane, washed with water and dried over Na_2SO_4. A white solid was obtained by evaporation of the solvent, which was pure according to NMR spectroscopic analysis (56 mg, 0.19 mmol, 100 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, $J_{1,3/7,9}$ = 1.5 Hz, 2 H, H–3/9), 6.82 (d, $J_{1,3/7,9}$ = 1.5 Hz, 2 H, H–1/7), 4.55 (d, $J_{endo,exo}$ = 17.0 Hz, 2 H, H–6/12$_{exo}$), 4.26 (s, 2 H, NCH_2N), 3.93 (d, $J_{endo,exo}$ = 17.0 Hz, 2 H, H–

6/12$_{endo}$), 2.41 (s, 6 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0 (NC), 146.7 (C–4A/10A), 134.8 (C–4/10), 128.9 (C–1A/7A), 126.9 (C–3/9), 122.4 (C–1/7), 122.2 (C–2/8), 67.1 (NCH_2N), 54.6 (C–6/12), 17.0 (CH_3). IR (neat): $\tilde{\nu}$ = 2123 (s) cm^{-1} (NC). HRMS (ESI): m/z calcd. for $C_{19}H_{17}N_4^+$: 301.1448 [*M*+H]$^+$; found 301.1444.

Photophysical measurements

UV-vis absorption spectra were measured using a Shimadzu UV–3600 spectrophotometer in 1.00 cm optical pass quartz cuvettes with teflon caps. Baselines were obtained with pure solvents, slow spectral acquisition speed and 1 nm of spectral width. Concentrations were adjusted so that absorbances resulted of 0.05–0.40, in order to obtain acceptable signal/noise ratios and to minimize inner filter effects. Molar absorptivities were obtained from Lambert–Beer plots in each solvent. Even though the standard deviations associated to the linear regressions are lower, a 3% error is estimated due to solution preparation.

Emission and excitation spectra were obtained using a PTI QuantaMaster QM4 spectrofluorometer in 1.00 cm optical pass fluorescence quartz cuvettes with teflon caps in right angle geometry. Appropriate excitation and emission wavelengths were chosen for each case, and emission filters were used when necessary. Spectra were acquired with 0.2 s integration time and 1 nm steps. Slits were adjusted between 0.25 and 1.00 mm in order to obtain adequate signal/noise ratios but avoiding saturation of detection. Emission spectra were corrected using the mathematical function provided by the instrumental software.

Fluorescence quantum yield determination was performed using the relative method according to the guidelines suggested by the International Union of Pure and Applied Chemistry (IUPAC) and by Rurak.[2,3] Low absorbance (A < 0.1) solutions were used to avoid inner filter effects and errors produced by an uneven distribution of excited species in the detection volume. In every case the same cuvette was used for sample and reference and the excitation was performed at a wavelength were both compounds presented significant absorption and that allowed full registration of their emission spectra. If possible, an absorption maximum (or minimum) was chosen. Naphthalene in cyclohexane was the selected reference for compounds **2a**, **2c** and **2d**, and phenanthrene in ethanol was chosen for **2b**.[4,5] Quantum yields were obtained from the slope of the linear regression of the graph of the integrated emission intensity v. $1–10^{-A(\lambda)}$, where A(λ) is the absorbance at the excitation wavelength. At least four spectra for different absorbances in the 0 – 0.1 range were obtained, in

order to remove spurious light influence and to guarantee emission linearity with respect to absorption.

Fluorescence lifetimes were measured using the TCSPC technique in a HORIBA Jobin Yvon IBH spectrofluorometer equipped with a NanoLED HORIBA Jobin Yvon 282 nm laser diode with <100 ps pulse width and 1 MHz repetition frequency. The excitation monochromator was set in 282 nm and the emission monochromator was adjusted for each sample and solvent at its maximum fluorescence wavelength. Slits were set at their maximum aperture in both cases and a WG305 filter and a polarizer in the magic angle were used. Acquisition was performed with a Picosecond Photon Detection Module IBH TBX-04 (1024 channels, 55 ps/channel). The pulse was obtained using a scattering glass set at 45° instead of the sample with the excitation monochromator set at 287 nm and with slits fixed to avoid saturation of detection. Once the pulse and decays were registered, deconvolutions were performed using the DAS6 v6.3 – HORIBA Jobin Yvon software. A nonlinear least square method was employed for the fit of the decay data to a mono–exponential equation ($A + B1 \exp(t/\tau)$), and the quality of the fit was assessed through the value of χ^2 and a visual inspection of the autocorrelation function and the residuals.

References

1 L. Trupp, S. L. Laurella, M. C. Tettamanzi, B. C. Barja and A. C. Bruttomesso, *J. Mol. Struct.*, 2018, **1157**, 434–443.

2 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.

3 U. Resch-Genger and K. Rurack, *Pure Appl. Chem.*, 2013, **85**, 2005–2013.

4 K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9850–9860.

5 W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 1968, **3251**, 3251–3260.

2. NMR spectra of **2b**

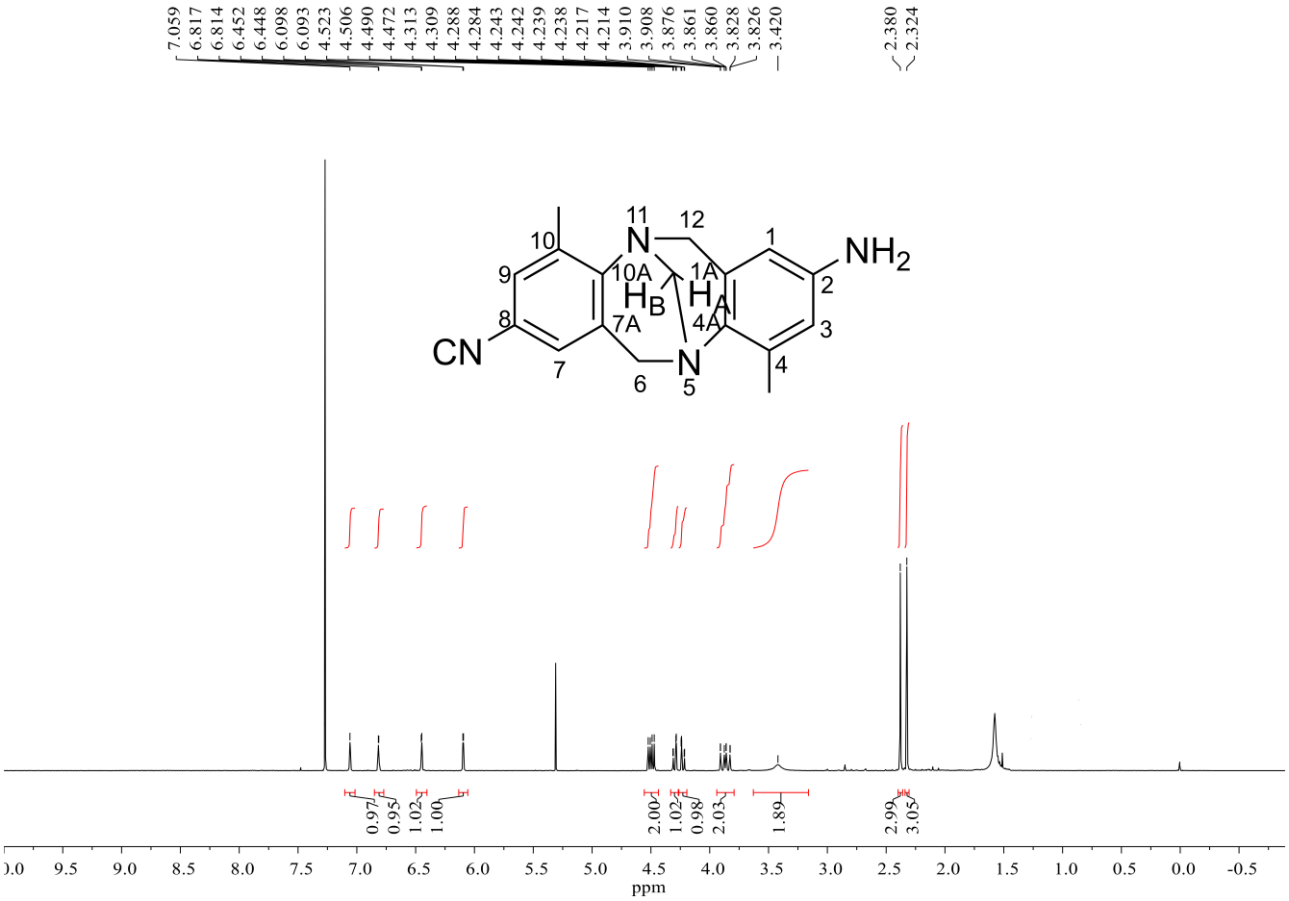

Figure S1. ^{1}H NMR spectrum of **2b** in $CDCl_3$ at 25 ˚C (500 MHz).

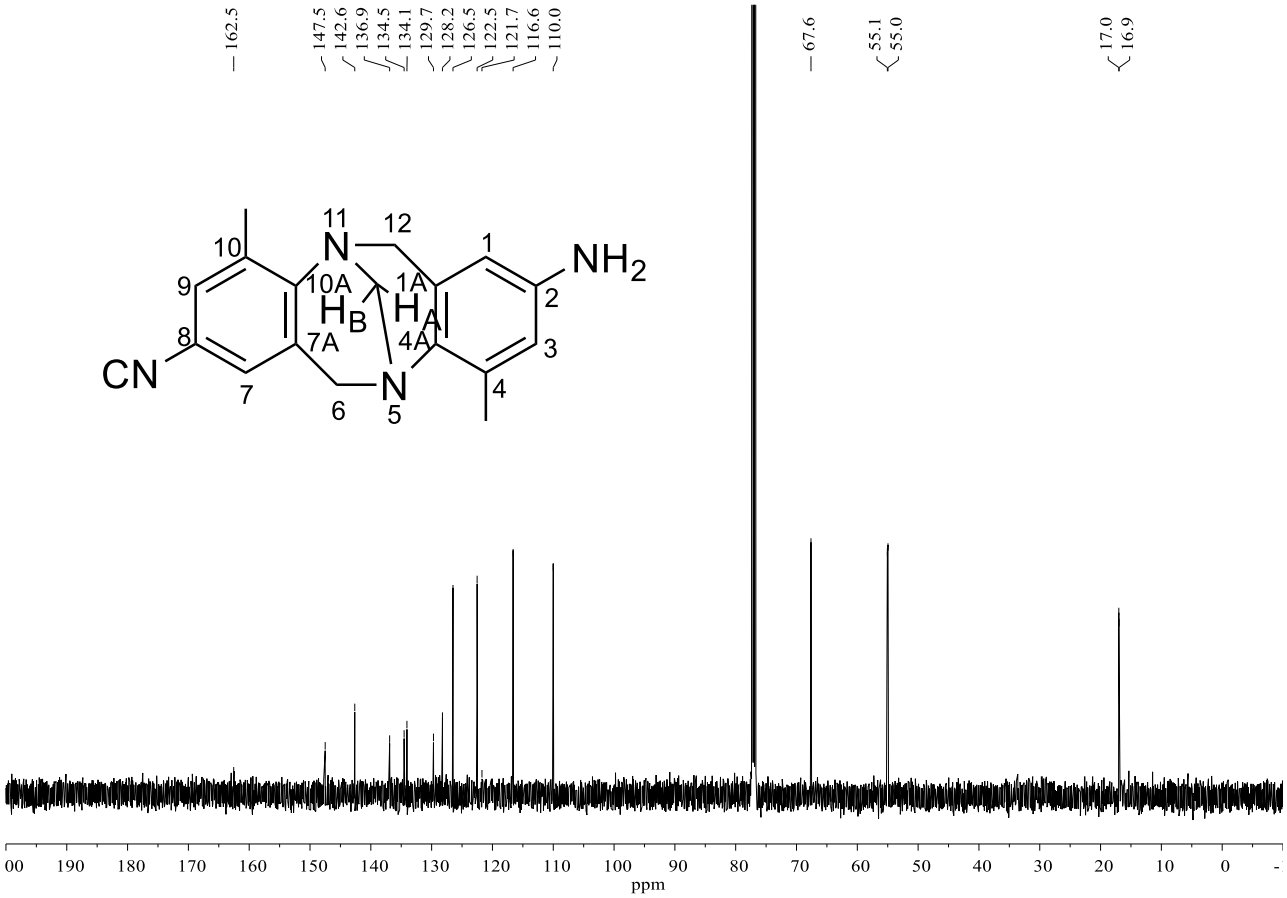

Figure S2. ^{13}C NMR spectrum of **2b** in $CDCl_3$ at 25 ˚C (125 MHz).

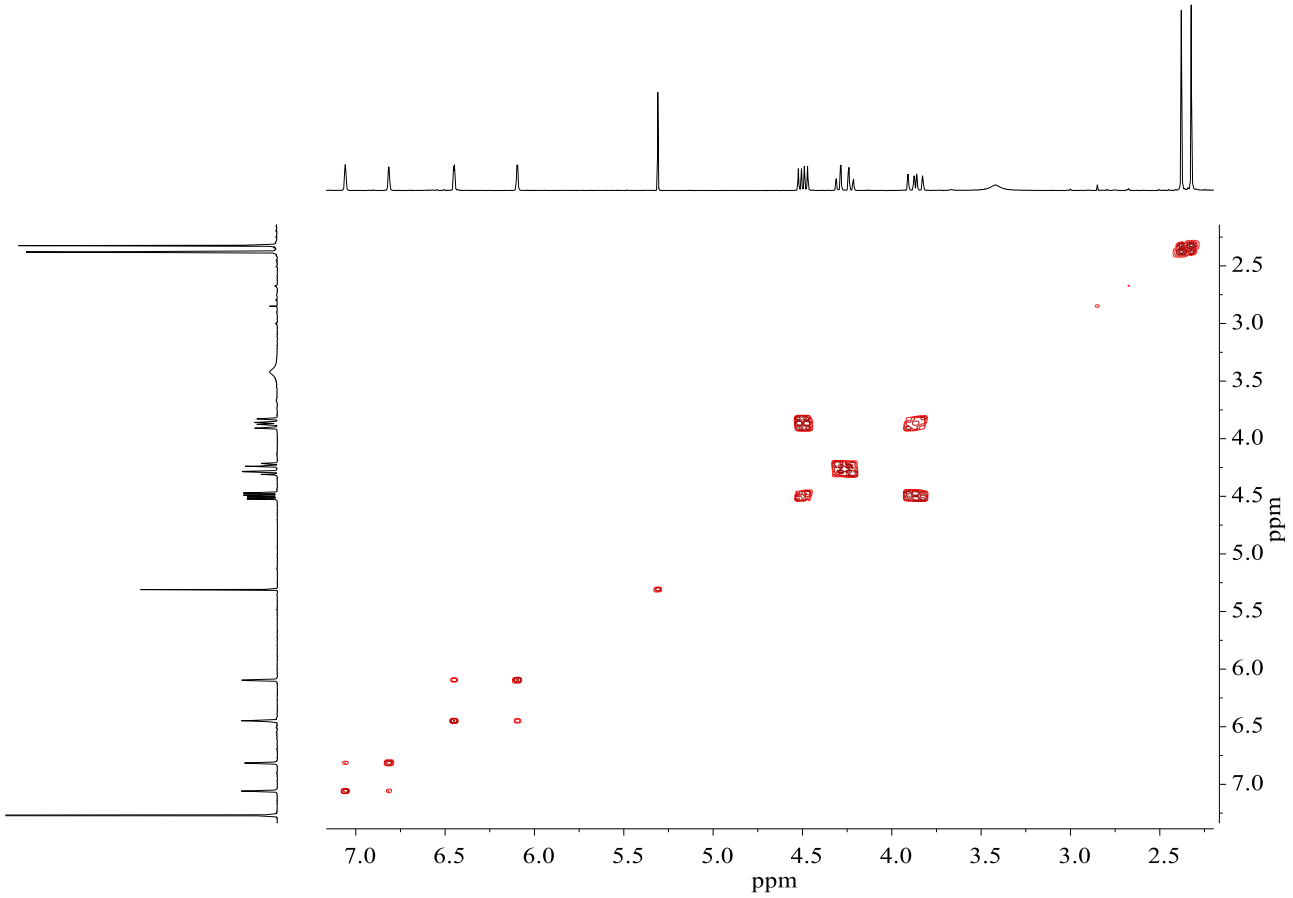

Figure S3. COSY NMR spectrum of **2b** in $CDCl_3$ at 25 ˚C (500 MHz for ^{1}H).

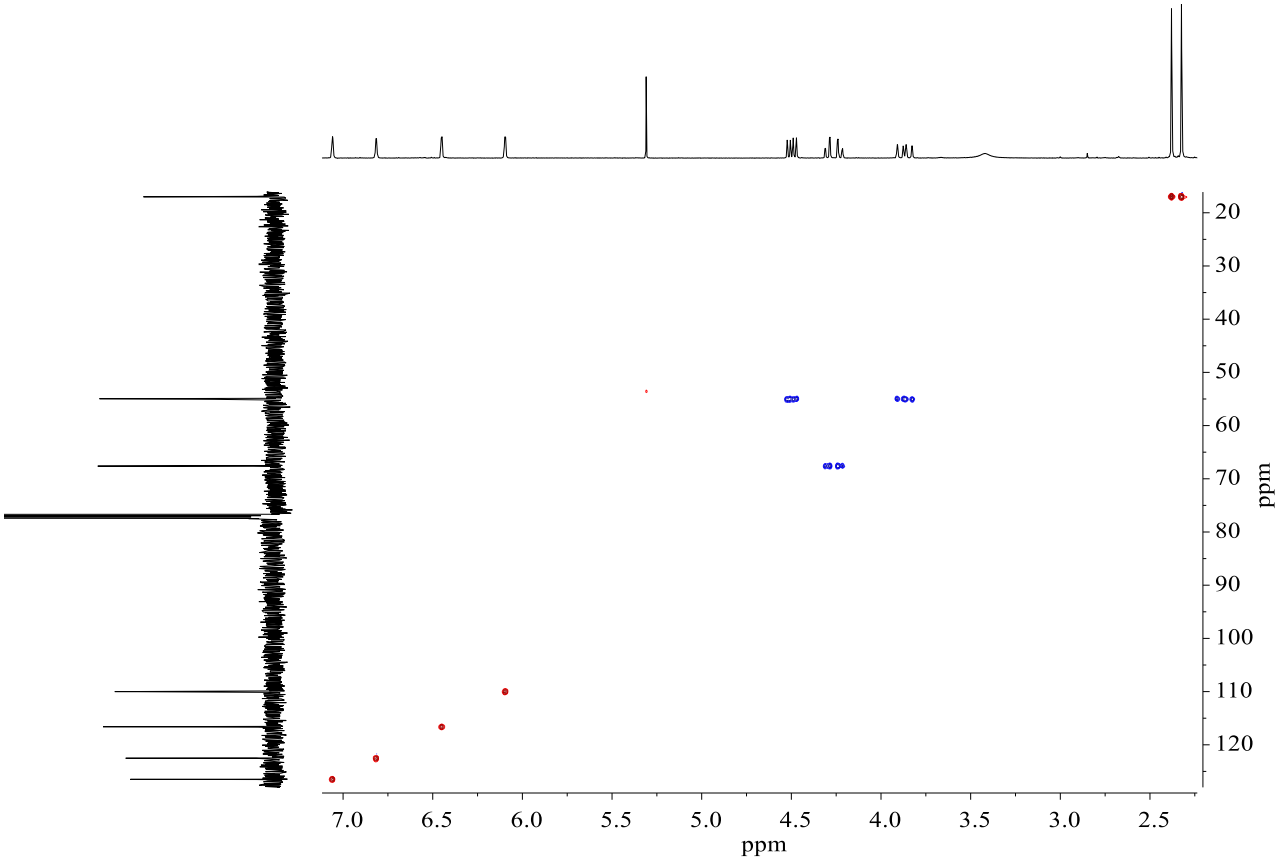

Figure S4. HSQC–DEPT NMR spectrum of **2b** in $CDCl_3$ at 25 ˚C (500 MHz for ^1H).

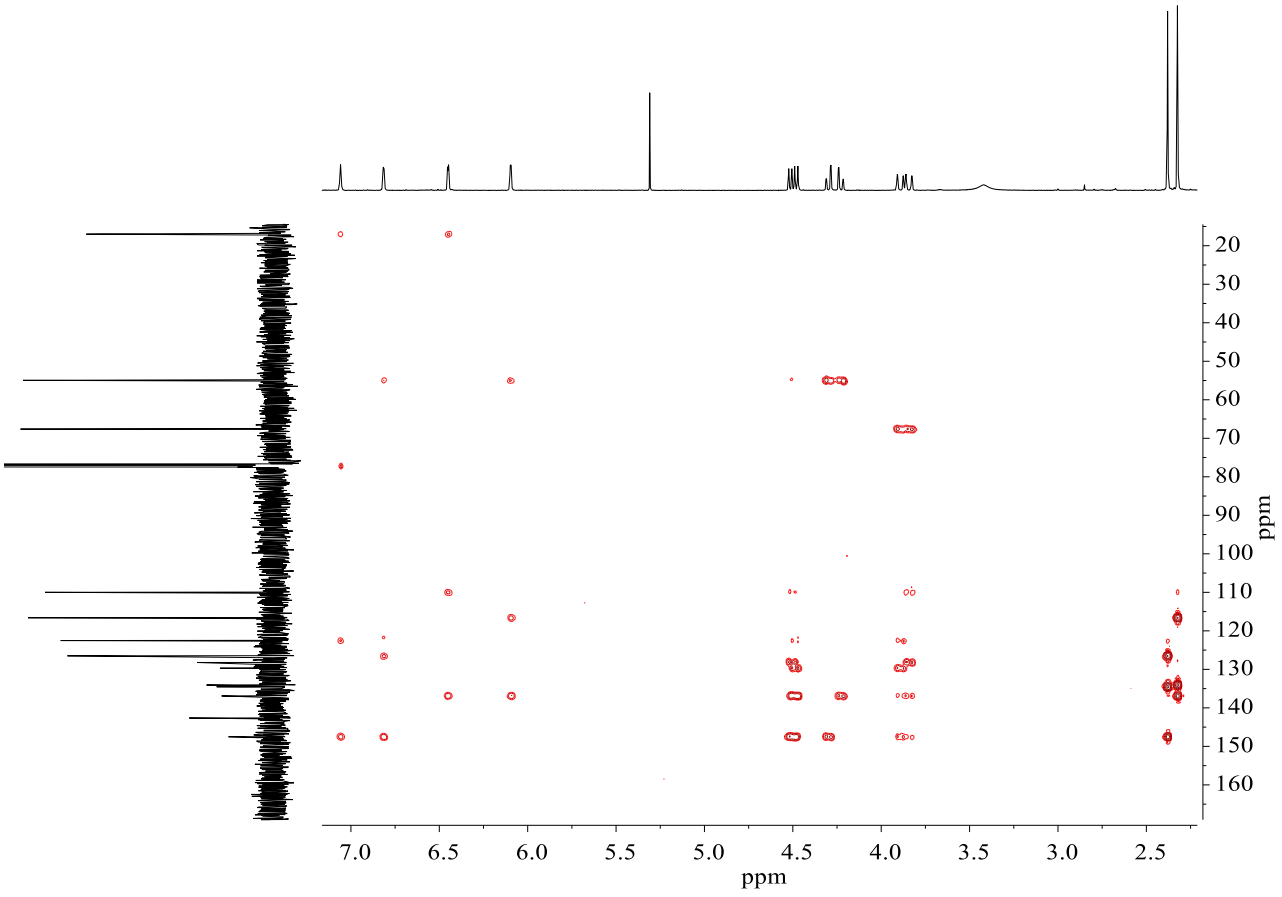

Figure S5. HMBC NMR spectrum of **2b** in $CDCl_3$ at 25 ˚C (500 MHz for ^1H).

3. Comparison of NMR spectra of **2b** with **2a** and **2c**

Table S1. ^{1}H and ^{13}C NMR signals of **2a**–**c** and chemical shift difference between the asymmetrical (**2b**) and dissymmetrical (**2a** / **2c**) compounds.

	δ (^{1}H) / ppm			δ (^{13}C) / ppm		
	2a / **2c**	**2b**	Δδ	**2a** / **2c**	**2b**	Δδ
1	6.09 *2a*	6.10	0.01	110.4 *2a*	110.0	–0.4
2	–	–	–	142.3 *2a*	142.6	0.3
3	6.41 *2a*	6.45	0.04	116.3 *2a*	116.6	0.3
4	–	–	–	133.8 *2a*	134.1	0.3
7	6.82 *2c*	6.82	0.00	122.4 *2c*	122.5	0.1
8	–	–	–	122.2 *2c*	121.7	–0.5
9	7.09 *2c*	7.06	–0.03	126.9 *2c*	126.5	–0.4
10	–	–	–	134.8 *2c*	134.5	–0.3
1A	–	–	–	129.0 *2a*	128.2	–0.8
4A	–	–	–	137.7 *2a*	136.9	–0.8
7A	–	–	–	128.9 *2c*	129.7	0.8
10A	–	–	–	146.7 *2c*	147.5	0.8
6_{endo}	3.93 *2c*	3.89	–0.04	54.6 *2c*	55.0	0.4
6_{exo}	4.55 *2c*	4.49	–0.06			
12_{endo}	3.80 *2a*	3.84	0.04	55.4 *2a*	55.1	–0.3
12_{exo}	4.45 *2a*	4.51	0.06			
NCH_2N	4.27 *2a*	4.23	–0.04	68.1 *2a*	67.6	0.5
	4.26 *2c*	4.30	0.04	67.1 *2c*		–0.5
C_{10}–$\underline{CH_3}$	2.41 *2c*	2.38	–0.03	17.0 *2c*	16.9	–0.1
C_4–$\underline{CH_3}$	2.31 *2a*	2.32	0.01	17.0 *2a*	17.0	0.0
NH_2	3.37 *2a*	3.42	0.05	–	–	–
NC	–	–	–	163.0 *2c*	162.5	–0.5

4. IR spectra assignment of **2a–d**

Table S2. IR signals (in cm^{-1}) of **2a–d**. ν: stretching, δ: in plane deformation, γ: out of plane deformation; vs: very strong, s: strong, m: medium, w: weak, vw: very weak, b: broad, ot: overtone, n.d.: not determined

Assignment	**2a**	**2b**	**2c**	**2d**
ν_a NH_2	3417 (w, b)	3438 (w, b)	–	–
ν_s NH_2	3318 (w, b) (3203, ot)	3348 (w, b) (3226, ot)	–	–
ν NH amide	–	–	–	3298 (w, b)
ν C-H $_{aliph.}$	2950, 2891, 2842 (vw, b)	2950, 2922, 2852 (vs, b)	2954, 2922, 2852 (w, b)	2942, 2885, 2843 (vw)
ν C-H_{arom}	n.d.	n.d.	n.d.	3194, 3134, 3072 (vw)
ν N≡C	–	2125 (m)	2123 (s)	–
ν CO (I)	–	–	–	1660 (s)
δ NH_2	1612 (s, b)	1612 (s, b)	–	–
δ -NH- amide	–	–	–	1608
ν C=C-C ring range, δ CH_2, CH_3	1323–1479	1323–1467	1330–1471	1321–1477
δ NH / ν CN (II)	–	–	–	1547
ν CN tertiary amine	1213	1213	1215	1205
ρ CH_3	1072	1072	1072	1070
δ =C-H	918	914	914	916
γ =C-H	652	652	652	649
γ NH/CN (amide V)	–	–	–	712 (m, b)

5. Photophysical data of the UV-vis spectra of **2a–d**

Table S3. Relevant photophysical data of the UV-vis spectra of TBs **2a–d** in different solvents. λ_{max1} is the wavelength of the principal absorption peak, λ_{max2} is the wavelength of the red–shifted absorption peak and ε_1 and ε_2 are the respective molar absorption coefficients.

TB	Solvent	λ_{max1} / nm	ε_1 [a] / $M^{-1}cm^{-1}$	λ_{max2} / nm	ε_2 [a] / $M^{-1}cm^{-1}$
2a	Hexane	247	[b]	308	[b]
	Dichloromethane	250	1.5×10^4	310	4.1×10^3
	Acetonitrile	250	1.7×10^4	310	4.2×10^3
	Methanol	247	1.6×10^4	304	3.7×10^3
2b	Hexane	250	[b]	292 [c]	[b]
	Dichloromethane	247	1.4×10^4	299 [c]	4.8×10^3
	Acetonitrile	250	1.6×10^4	295 [c]	5.3×10^3
	Methanol	246	1.3×10^4	286 [c]	4.8×10^3
2c	Hexane	239	[b]	269	[b]
	Dichloromethane	243	1.6×10^4	272	1.1×10^4
	Acetonitrile	242	1.4×10^4	270	1.1×10^4
	Methanol	241	1.3×10^4	269	9.8×10^3
2d	Hexane	[b]	[b]	[b]	[b]
	Dichloromethane	266	2.0×10^4	–	–
	Acetonitrile	265	2.1×10^4	–	–
	Methanol	263	2.2×10^4	–	–

[a] 3 % error is estimated due to sample preparation. [b] Not obtained due to low solubility. [c] Estimated by spectral deconvolution.

6. Lifetime measurements of **2a–c** in acetonitrile

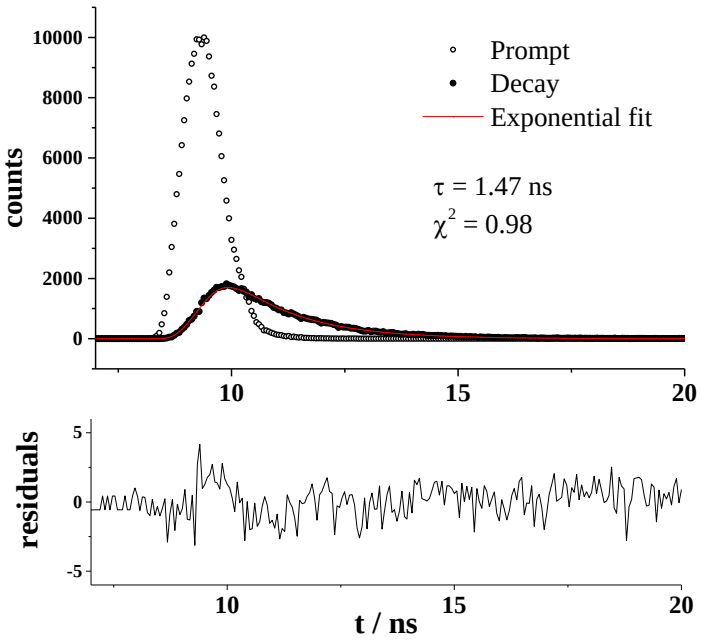

Figure S6. Fluorescence decay of **2a** in acetonitrile (λ_{exc} = 282 nm, λ_{em} = 350 nm)

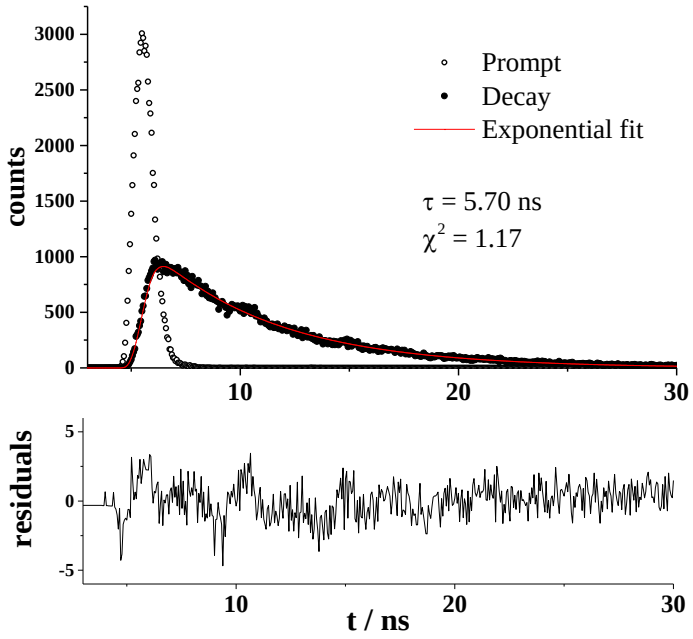

Figure S7. Fluorescence decay of **2b** in acetonitrile (λ_{exc} = 282 nm, λ_{em} = 416 nm)

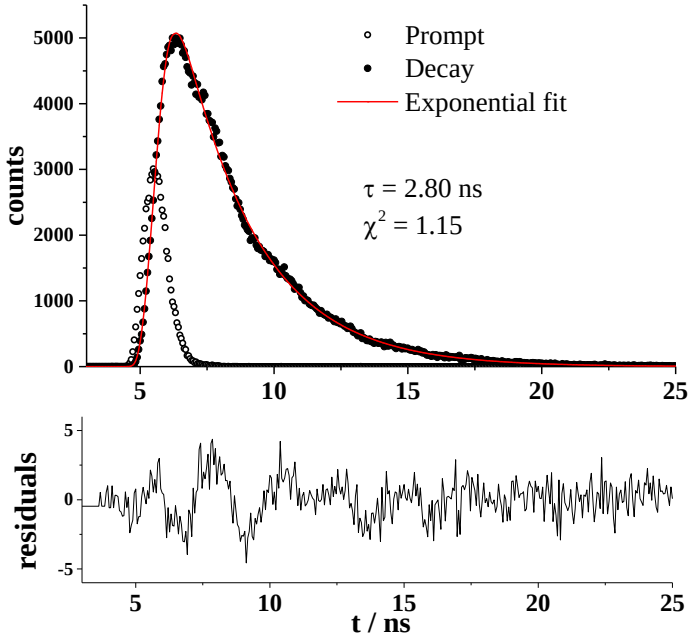

Figure S8. Fluorescence decay of **2c** in acetonitrile (λ_{exc} = 282 nm, λ_{em} = 400 nm)

Table S4. Relevant data from lifetime measurements of TBs **2a**–**c** in acetonitrile (λ_{exc} = 282 nm). λ_{em} is the analyzed emission wavelength, A is the offset, B1 is the pre–exponential factor, τ is the fluorescence lifetime and χ^2 is the chi-square of the fit.

TB	λ_{em} / nm	A		B1		τ / ns		χ^2
		value	SD	value	SD	value	SD	
2a	350	0.55	0.05	0.01463	0.00005	1.470	0.006	0.975
2b	416	0.31	0.06	0.01859	0.00006	5.70	0.02	1.171
2c	400	0.47	0.04	0.1200	0.0002	2.801	0.005	1.146

7. Parameters of the Lippert–Mataga plots of **2a**–**c**

Table S5. Parameters for the linear regressions of the Lippert–Mataga plots of TBs **2a**–**c**. A is the intercept, B is the slope and R^2 is the R–square of the fit.

TB	A / 10^4		B / 10^4		R^2
	value	SD	value	SD	
2a	0.20	0.03	0.8	0.1	0.86
2b	1.32	0.01	1.13	0.05	0.97
2c	0.680	0.008	1.51	0.04	0.98