

Chemical Communications

Cation-triggered “switching on” of the near infra-red (NIR) fluorescence of rigid fluorophore–spacer–receptor ionophores

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Supplementary Information

Materials. All the solvents employed were of spectroscopic grade and purchased from Aldrich. Metal perchlorates obtained from Merck, Acros, and Aldrich were of highest purity available and dried in a vacuum oven before use.¹ For the determination of the complex stability constants, acetonitrile was distilled from CaH₂ prior to use. The starting materials for the synthesis of **1–4** were obtained from Merck and Aldrich. The chemical structures of the dyes were confirmed by elemental analysis and ¹H NMR and their purity was checked by reversed phase HPLC (HPLC set up from Merck-Hitachi; RP18 column; acetonitrile/water = 75/25 as eluent) employing UV detection (UV detector from Knauer; fixed wavelength at 310 nm). NMR spectra were obtained with a 500 MHz NMR spectrometer Varian Unity_{plus} 500. The melting points (mp) measured with a digital melting point analyzer IA 9100 (Kleinfeld GmbH) are uncorrected.

Synthesis. General procedures. For the *N*-phenyl-1,8-naphthalimide-containing chalcones **A–D**, a mixture of 4-acetylnaphthalic acid phenylamide (2 mmol for **C**, 1 mmol for **A**, **B**, **D**) the respective benzaldehyde (2 mmol benzaldehyde for **C**, 1 mmol 4-(1,4,7,10-tetrathia-13-aza-cyclopentadec-13-yl)-benzaldehyde, 4-(1,4,7,10-tetraoxa-13-aza-cyclopentadec-13-yl)-benzaldehyde, *N,N*-dimethyl-amino-benzaldehyde for **A**, **B** and **D**) and piperidine was refluxed in absolute ethanol for 8–10 h. After cooling, a solid precipitate was separated, washed with ethanol, purified by column chromatography (silica, dichloromethane, chloroform) and recrystallized. **1–4** were prepared by heating a solution of 1 mmol of the corresponding chalcone and 2 mmol phenylhydrazine hydrochloride in 5 ml acetic acid for 10 h at 100°C. The resulting red reaction mixture was poured into 50 ml ice water and neutralized with 10 % aqueous sodium carbonate. The solid precipitate was separated and washed with water. The product was purified by column chromatography (silica/toluene, then CHCl₃). After evaporation of the solvent, the Δ^2 -pyrazoline was crystallized from the appropriate solvent.

3-[4-(1,4,7,10-Tetrathia-13-aza-cyclopentadec-13-yl)phenyl]-1-(N-phenyl-1,8-naphthalimid-4-yl)-prop-2-en-1-one (**A**). Yield 25 %; mp 155–157°C (from toluene). Elemental analysis (found: C, 64.92; H, 5.25; N, 4.15; S, 18.64. Calc. for C₃₇H₃₆N₂O₃S₄: C, 64.87; H, 5.30; N, 4.09; S, 18.72). ¹H NMR (CDCl₃) δ(ppm): 2.764–2.820 (-CH₂-S, m, 16 H), 3.613–3.665 (>N-CH₂, t, *J* = 7.9 Hz, 4 H), 6.624–6.654 (2 Ar-H (C₆H₄), d, *J* = 9 Hz), 7.452–7.483 (2 Ar-H (C₆H₄), d, *J* = 9 Hz), 7.066–7.118 and 7.549–7.603 (-CH=CH-, 2 × d, *J* = 15.9 Hz, 2 × 1 H), 7.155–8.714 (Ar-H, m). ¹³C NMR (CDCl₃) δ(ppm): 29.068, 32.388, 32.806, 32.951(-CH₂-S-), 52.003 (-CH₂N<), 111.755, 121.988, 122.623, 122.913, 124.175, 125.292, 126.458, 127.889, 128.218, 128.580, 128.813, 129.030, 129.432, 130.534, 131.233, 131.964, 143.814, 148.524, 149.151 (arom. C and -CH=CH-), 163.852 and 164.168 (>C=O, amide), 194.482 (>C=O, ketone).

3-[4-(1,4,7,10-Tetraoxa-13-aza-cyclopentadec-13-yl)phenyl]-1-(N-phenyl-1,8-naphthalimid-4-yl)-prop-2-en-1-one (**B**). Yield 33 %; mp 112–115°C (from acetonitrile). Elemental analysis (found: C, 71.41; H, 5.68; N, 4.43. Calc. for C₃₇H₃₆N₂O₇: C, 71.59; H, 5.84; N, 4.51). ¹H NMR (CDCl₃) δ(ppm): 3.630–3.678 (-CH₂-O, m, 16 H), 3.758–3.796 (>N-CH₂, t, *J* = 6 Hz, 4 H), 6.658–6.686 (2 Ar-H (C₆H₄), d, *J* = 9 Hz), 7.424–7.452 (2 Ar-H (C₆H₄), d, *J* = 9 Hz), 7.042–7.094 and 7.499–7.551 (-CH=CH-, 2 × d, *J* = 15.9 Hz, 2 × 1 H), 7.161–8.715 (Ar-H, m). ¹³C NMR (CDCl₃) δ(ppm): 52.811 (-CH₂N<), 68.190, 69.998, 70.288, 71.292 (-CH₂-O-), 111.752, 121.197, 121.575, 122.853, 123.987, 126.350, 127.789, 128.496, 128.569, 129.397, 131.061, 131.913, 132.652, 135.217, 144.124, 149.148, 150.434 (arom. C and -CH=CH-), 163.861 and 164.189 (>C=O, amide), 194.527 (>C=O, ketone).

1-(N-phenyl-1,8-naphthalimid-4-yl)-3-phenyl-prop-2-en-1-one (**C**). Yield 50 %; mp 181–182°C (from nitromethane). Elemental analysis (found: C, 80.25; H, 4.15; N, 3.64. Calc. for C₂₇H₁₇NO₃: C, 80.38; H, 4.25; N, 3.47). ¹H NMR (CDCl₃) δ(ppm): 7.290–8.733 (arom. and -CH=CH-, m). ¹³C NMR (CDCl₃) δ(ppm): 122.997, 124.715, 126.255, 126.842, 128.175, 128.556, 128.738, 128.861, 129.016, 129.163, 129.445, 130.385, 131.444, 132.071, 132.337, 133.984, 135.118, 142.657, 148.049 (arom. and -CH=CH-), 163.729 and 164.066 (>C=O, amide), 194.427 (>C=O, ketone).

3-[4-(Dimethylamino)phenyl]-1-(N-phenyl-1,8-naphthalimid-4-yl)-prop-2-en-1-one (**D**). Yield 67 %; mp 213–215°C (from nitromethane). Elemental analysis (found: C, 77.91; H, 4.81; N, 6.23. Calc. for C₂₉H₂₂N₂O₃: C, 78.01; H, 4.97; N, 6.27). ¹H NMR (CDCl₃) δ(ppm): 3.058 (CH₃, s, 3 H), 6.658–6.688 (2 Ar-H, d, *J* = 8.9 Hz), 7.515–7.548 (2 Ar-H, d, *J* = 8.9 Hz), 7.052–7.105 and 7.464–7.515 (-CH=CH-, 2 × d, *J* = 15.7 Hz, 2 × 1 H), 7.329–8.712 (Ar-H, m). ¹³C NMR (CDCl₃) δ(ppm): 40.081 (H₃C-N), 111.804, 121.232, 121.541, 122.882, 124.005, 126.362, 127.802, 128.588, 128.790, 128.968, 129.246, 129.417, 130.567, 130.925, 131.928, 132.670, 135.237, 144.157,

149.331, 152.588 (arom. and $-\text{CH}=\text{CH}-$), 163.908 and 164.209 ($>\text{C}=\text{O}$, amide), 194.546 ($>\text{C}=\text{O}$, ketone).

1-Phenyl-3-(N-phenyl-1,8-naphthalimid-4-yl)-5-[4-(1,4,7,10-tetrathia-13-aza-cyclopentadec-13-yl)-phenyl]- Δ^2 -pyrazoline (1). Yield 24 %; mp 215–216°C (from acetic acid). Elemental analysis (found: C, 66.75; H, 5.28; N, 7.35. Calc. For $\text{C}_{43}\text{H}_{42}\text{N}_4\text{O}_2\text{S}_4$: C, 66.63; H, 5.46; N, 7.23). ^1H NMR (CDCl_3) δ (ppm): 2.759–2.810 ($-\text{CH}_2-\text{S}$, m, 16 H), 3.371–3.417 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 3.615–3.670 ($>\text{N}-\text{CH}_2$, t, $J = 7.9$ Hz, 4 H), 4.020–4.080 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 5.333–5.395 (Ar-CHN, dd, 1 H), 6.922–10.056 (Ar-H, m, 19 H). ^{13}C NMR (CDCl_3) δ (ppm): 29.102, 32.390, 32.812, 33.025 ($-\text{CH}_2-\text{S}-$), 45.202 (CH_2 pyrazoline), 52.003 ($-\text{CH}_2\text{N}$), 63.417 (Ar-CHN), 113.722, 120.402, 121.774, 122.640, 126.186, 126.920, 127.688, 128.312, 128.652, 128.978, 129.046, 129.156, 129.360, 129.521, 131.105, 131.521, 134.900, 135.440, 135.648, 143.770, 145.297 (arom. C), 164.009 and 164.522 ($\text{C}=\text{O}$ amide).

1-Phenyl-3-(N-phenyl-1,8-naphthalimid-4-yl)-5-[4-(1,4,7,10-tetraoxa-13-aza-cyclopentadec-13-yl)-phenyl]- Δ^2 -pyrazoline (2). Yield 24 %; mp 187–191°C (from toluene). Elemental analysis (found: C, 72.42; H, 5.88; N, 7.92. Calc. For $\text{C}_{43}\text{H}_{42}\text{N}_4\text{S}_6$: C, 72.66; H, 5.96; N, 7.88). ^1H NMR (CDCl_3) δ (ppm): 3.375–3.421 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 3.569–3.658 ($-\text{CH}_2-\text{O}$, m, 16 H), 3.713–3.737 ($>\text{N}-\text{CH}_2$, t, $J = 6.1$ Hz, 4 H), 4.027–4.085 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 5.330–5.368 (Ar-CHN, dd, 1 H), 6.883–10.060 (Ar-H, m, 19 H). ^{13}C NMR (CDCl_3) δ (ppm): 45.182 (CH_2 pyrazoline), 52.652 ($-\text{CH}_2\text{N}$), 63.267 (Ar-CHN), 68.443, 70.039, 70.225, 71.266 ($-\text{CH}_2\text{O}-$), 114.017, 120.294, 121.642, 122.840, 126.188, 126.891, 127.758, 128.220, 128.647, 128.985, 129.033, 129.157, 129.353, 129.517, 131.065, 131.546, 134.890, 135.437, 135.652, 143.647, 145.301 (arom. C), 164.025 and 164.528 ($\text{C}=\text{O}$ amide).

1,5-Diphenyl-3-(N-phenyl-1,8-naphthalimid-4-yl)- Δ^2 -pyrazoline (3). Yield 28 %; mp 238–239°C (from toluene). Elemental analysis (found: C, 80.51; H, 4.45; N, 8.78. Calc. For $\text{C}_{33}\text{H}_{23}\text{N}_3\text{O}_2$: C, 80.31; H, 4.70; N, 8.51). ^1H NMR (CDCl_3) δ (ppm): 3.395–3.473 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 4.089–4.186 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 5.413–5.477 (Ar-CHN, dd, 1 H), 6.882–10.066 (Ar-H, m, 20 H). ^{13}C NMR (CDCl_3) δ (ppm): 45.124 (CH_2), 63.618 (Ar-CHN), 113.924, 120.510, 121.906, 122.883, 125.795, 126.279, 127.874, 127.989, 128.620, 128.691, 128.989, 129.215, 129.374, 131.985, 131.611, 134.766, 135.297, 135.377, 141.634, 143.467, 145.296 (C arom.), 163.976 and 164.472 ($\text{C}=\text{O}$ amide).

1-Phenyl-3-(N-phenyl-1,8-naphthalimid-4-yl)-5-[4-(N,N-dimethylamino)-phenyl]- Δ^2 -pyrazoline (4). Yield 36 %; mp 225–226°C (from toluene). Elemental analysis (found: C, 78.25; H, 5.17; N, 10.64. Calc. For $\text{C}_{35}\text{H}_{28}\text{N}_4\text{O}_2$: C, 78.34; H, 5.25; N, 10.44). ^1H NMR (CDCl_3) δ (ppm): 2.931 [$-\text{N}(\text{CH}_3)_2$, s, 6 H], 3.367–3.445 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 4.018–4.115 ($\text{CH}_2\text{C}=\text{N}$, dd, 1 H), 5.335–5.400

(Ar-CHN, dd, 1 H), 6.684–10.074 (Ar-H, m, 19 H). ^{13}C NMR (CDCl_3) δ (ppm): 40.478 (CH_3N), 45.144 (CH_2), 63.324 (Ar-CHN), 112.944, 114.007, 120.296, 121.645, 122.843, 126.172, 126.691, 127.767, 128.219, 128.640, 128.989, 129.048, 129.136, 129.358, 129.516, 131.056, 131.556, 134.893, 135.428, 135.639, 143.637, 145.292 (C arom.), 164.027 and 164.531 (C=O amide).

Steady-state absorption and fluorescence spectroscopy. UV/Vis-spectra were recorded on a Carl Zeiss Specord M400/M500 absorption spectrometer and steady-state emission spectra on a Spectronics Instruments 8100 spectrofluorometer. For the fluorescence experiments, only dilute solutions with an optical density (OD) below 0.01 at the excitation wavelength (OD < 0.04 at the absorption maximum) were used in order to avoid reabsorption effects. The relative fluorescence quantum yields (ϕ_f) were determined by adjusting the optical densities of the solutions at the excitation wavelengths to 0.1 ± 0.001 in a 100 mm absorption cell. These solutions were then transferred to a 10 mm fluorescence quartz cell. The fluorescence measurements were performed with a 90° standard geometry, an excitation polarizer set at 0° and an emission polarizer set at 54.7° . Fluorescein 27 in 0.1 N NaOH ($\phi_f = 0.90 \pm 0.03$)² was used as fluorescence standard. All the fluorescence spectra presented here are corrected for the spectral response of the detection system (calibrated quartz halogen lamp placed inside an integrating sphere; Gigahertz-Optik) and for the spectral irradiance of the excitation channel (calibrated silicon diode mounted at a sphere port; Gigahertz-Optik). The fluorescence quantum yields were calculated from 6 independent measurements and the uncertainties of the measurement were determined to $\pm 5\%$ (for $1.0 > \phi_f > 0.2$), $\pm 10\%$ (for $0.2 > \phi_f > 0.02$), and $\pm 20\%$ (for $0.02 > \phi_f$), respectively.

Time-resolved fluorescence spectroscopy. Fluorescence lifetimes (τ_f) were measured employing a unique laser impulse fluorometer with ps time resolution described elsewhere.³ The sample was excited with the second harmonic output (LBO crystal) of a regenerative mode-locked argon ion laser-pumped Ti:Sapphire laser at a repetition rate of 4 MHz (reduction by synchronized pulse selection). The fluorescence was collected at right angles (emission polarizer set at 54.7° ; monochromator with spectral bandwidths of 4, 8, and 16 nm) and the fluorescence decays were recorded with a time-correlated single photon counting setup and a time division of 5.2 ps chn^{-1} (experimental accuracy of $\pm 3 \text{ ps}$). The laser beam was attenuated using a double prism attenuator from LTB and typical excitation energies were in the nanowatt to microwatt range (average laser power). The excitation energies were checked and adjusted with a calibrated Si diode (Model 221 with 100:1 attenuator 2550, Graseby) and an optometer (Model S370, Graseby). In a typical experiment, the pulse peak power was $5 \times 10^{-2} \text{ W}$. For example, concerning a typical measurement

with excitation at 480 nm the sample was excited with *ca.* 10^5 photons per pulse. The instrumental response function (IRF) of the system was typically 30 ps (full width at half maximum). Temporal calibration of the experimental setup was checked with pinacyanol in ethanol ($\tau_f = 13 \text{ ps} \pm 1 \text{ ps}$),⁴ rose bengal in methanol ($\tau_f = 0.50 \text{ ns} \pm 0.02 \text{ ns}$),⁵ and fluorescein 27 in 0.1 N NaOH ($\tau_f = 4.50 \text{ ns} \pm 0.03 \text{ ns}$).⁶ For the estimation of the color shift (wavelength-dependent temporal response of the detection system) between the instrumental response function and the actual fluorescence decay, the fluorescence of fluorescein 27 (in 0.1 N NaOH) or (4-dicyanomethylene-2-methyl-6-*p*-dimethylamino-styryl-4H-pyran (DCM in methanol) were quenched by saturation with potassium iodide and the resulting decay profiles were recorded at the corresponding emission wavelengths. The fluorescence decay profiles were analyzed with a PC using the software package Global Unlimited V2.2 (Laboratory for Fluorescence Dynamics, University of Illinois). The accuracy of the fit of the single decays, as judged by reduced chi-squared (χ_R^2), the autocorrelation function $C(j)$ of the residuals, and the Durbin Watson parameter (DW), was always acceptable yielding values of $\chi_R^2 < 1.2$ and $DW > 1.8$, respectively.

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