

Electronic Supplementary Information

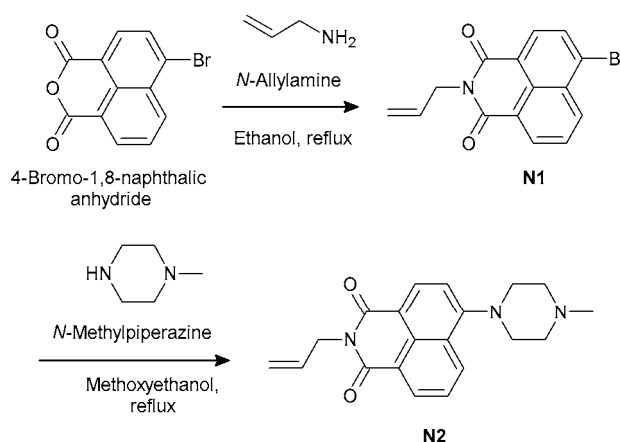
Fluorescent Nanoparticles for Ratiometric pH-Monitoring in the Neutral Range

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Supplementary Experimental Section.

Synthesis of the Polymerisable pH-Indicator.

The synthesis of the pH-indicator dye **N2** was done in a comparable procedure to the reported method of Niu *et al.*¹ (Scheme 1).



Scheme 1 Synthesis of the polymerisable pH-indicator dye **N2**.

Synthesis of *N*-Allyl-4-bromo-1,8-naphthalimide (**N1**).

1 g (3.4 mmol) of 4-bromo-1,8-naphthalic anhydride was suspended in 25 mL of absolute ethanol and heated up to 70 °C. Upon addition of 330 μ l (4.4 mmol) of allyl amine the reaction mixture turned brown. Afterwards the mixture was heated under reflux until the starting compound was completely dissolved. After 30 minutes of stirring the product precipitated and the reaction was refluxed for further 2 hours. The reaction was cooled to room temperature and the solid product was filtered, washed with ethanol and dried *in vacuo*. The product was purified by recrystallization from ethanol. Yield: pale brown needles (0.98 g, 92%).
mp 152 °C (from EtOH).

Elemental analysis: Found: C, 57.1; H, 3.1; N, 4.4. Calc. for $C_{15}H_{10}N_1O_2Br$ (316.2): C, 57.2; H, 3.2; N, 4.5%.

NMR data: δ_H (400 MHz; $CDCl_3$) 8.65 (1 H, d, Ph), 8.56 (1 H, d, Ph), 8.41 (1 H, d, Ph), 8.03 (1 H, d, Ph), 7.84 (1 H, dd, Ph), 6.01 (1 H, m, -CH=), 5.34 (1 H, dd, =CH₂), 5.23 (1 H, dd, =CH₂), 4.80 (2 H, m, -CH₂-) ppm.

δ_C (100 MHz; $CDCl_3$) 163.3 (2 C), 133.3, 132.1, 132.0, 131.3, 131.1, 130.6, 130.3, 129.0, 128.1, 123.0, 122.2, 117.9, 42.5 ppm.

MS (EI): m/z 315 (M^{+} , 20%), 300 (M-15, base peak).

Synthesis of *N*-Allyl-4-(*N*-methylpiperazinyl)-1,8-naphthal-imide (**N2**).

0.47 g (1.5 mmol) of *N*-allyl-4-bromo-1,8-naphthalimide, 0.9 g (9 mmol) of *N*-methyl-piperazine and 1 mg ($9 \cdot 10^{-3}$ mmol) of hydroquinone were suspended in 10 mL of 2-methoxyethanol and refluxed for 4 hours at 140 °C until the reagents were dissolved. The conversion was controlled using TLC with dichloromethane/methanol 5:1 (v/v) as the eluent. The product was precipitated by pouring the dark yellow solution into 50 mL of an ice-water mixture. The yellow precipitate was filtered, washed with 20 mL of ethanol and dried *in vacuo*. The product was further purified by recrystallization from ethanol. Yield: yellow needles (0.24 g, 48%).
mp 166 °C (from EtOH).

Elemental analysis: Found: C, 71.6; H, 6.1; N, 12.4. Calc. for $C_{20}H_{21}N_3O_2$ (335.4): C, 71.6; H, 6.3; N, 12.5%.

NMR data: δ_H (250 MHz; $CDCl_3$) 8.55 (1 H, d, Ph), 8.49 (1 H, d, Ph), 8.39 (1 H, d, Ph), 7.66 (1 H, t, Ph), 7.19 (1 H, d, Ph), 5.98 (1 H, m, -CH=), 5.28 (1 H, dd, =CH₂), 5.17 (1 H, dd, =CH₂), 4.77 (2 H, d, -CH₂-), 3.29 (4 H, m, -CH₂-N), 2.73 (4 H, m, -CH₂-N), 2.42 (3 H, s, Me) ppm.

δ_C (63 MHz; $CDCl_3$) 164.2, 163.7, 156.0, 132.7, 132.4, 131.2, 130.3, 129.9, 126.1, 125.6, 123.1, 117.3, 116.5, 115.0, 55.1 (2 C), 53.0 (2 C), 46.1, 42.2 ppm.

MS (EI): m/z 335 (M^{+} , base peak).

Supplementary Spectra.

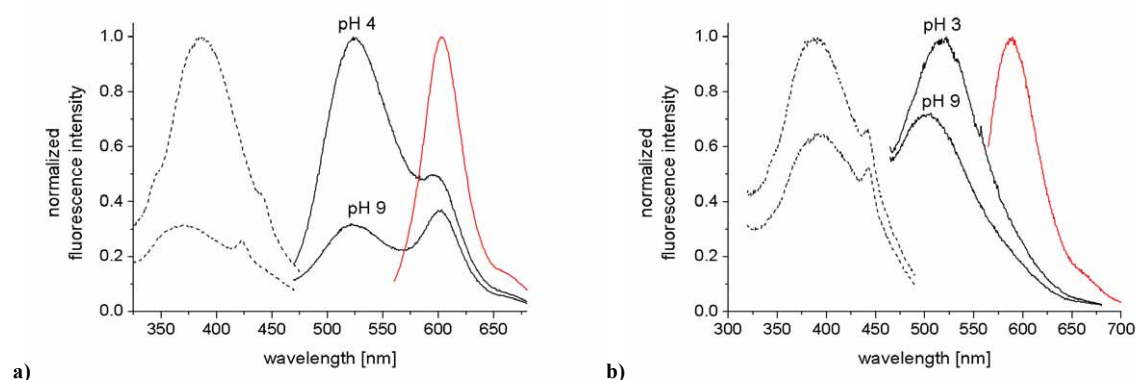


Fig.4 Excitation (dashed lines) and emission spectra (solid lines) of **N2** and **R3** inside **a)** the PAAm NPs ($\lambda_{\text{exc}} = 390$ nm, $\lambda_{\text{em}} = 520$ nm) and **b)** inside the core-shell NPs ($\lambda_{\text{exc}} = 390$ nm, $\lambda_{\text{em}} = 520$ nm). The fluorescence emission spectra of **R3** ($\lambda_{\text{exc}} = 543$ nm) are represented by the red curves.

Supplementary References.

¹ C.-G. Niu, G.-M. Zeng, L.-X. Chen, G.-L. Shen and R.-Q. Yu, *Analyst*, 2004, **129**, 20.