Electronic Supplementary Information (ESI)

Multiport logic operations triggered by protonation - a trisphenanthroline as a 3-Input AND – NOR – OR circuit

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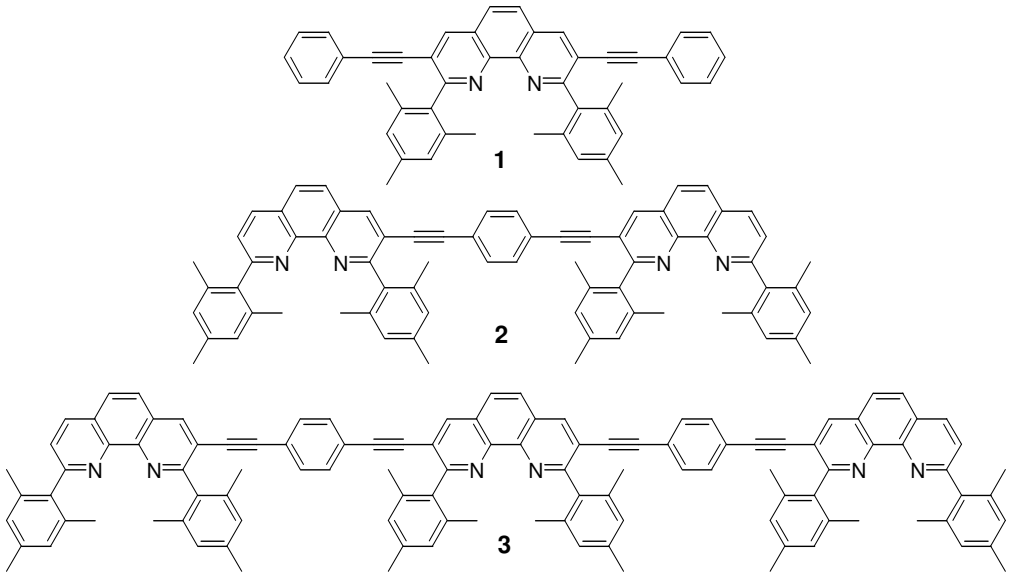
Chart S1. Compounds used for the present study.



Experimental:

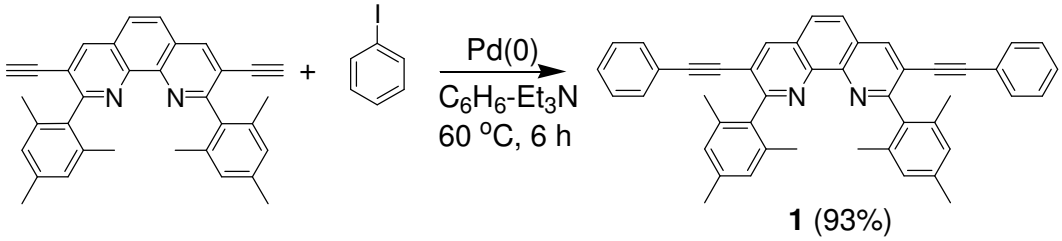
General. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance 400 (400 MHz). NMR analysis was conducted at room temperature in deuterated solvents. Positive ESI-MS spectra were recorded on the LCQ Deca Thermo Quest instrument, scanning over the *m/z* range 200-4000. Binding constants were calculated by using CH_2Cl_2-MeOH (4:1) as the solvent. In a typical run, 2.000 mL of a 1.0×10^{-5} M solution of the mixture of phenanthroline was taken and a solution of methanesulfonic acid (1.0×10^{-3} M) was added in small portions (5.00 μL). Absorption spectra were recorded at 25.0 (±0.1) °C taking into account the wave-length region from 250 nm to 700 nm. Fluorescence spectra were recorded at 25.0 (±0.1) °C taking into account the wavelength region from 350 nm to 700 nm. Subsequently, binding affinities were determined using the SPECFIT/32^{TM} [1]global analysis system by Spectrum Software Associates (Marlborough, MA). The SPECFIT program analyzes equilibrium data sets using singular value decomposition and linear regression modeling by the Levenberg-Marquardt method to determine cumulative binding constants. UV/Visible and Fluorescence spectra were recorded on a Varian Cary 100 Bio UV/visible Spectrometer and Varian Cary Eclipse Fluorescence Spectrometer, respectively. For fluorescence quantum yield

[1] a) H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta,* 1985, **32**, 257; b) H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta,* 1986, **33**, 943.

determination quininine sulphate was used as the standard (Φ_{Fl} = 0.54 in 1N H_2SO_4, Irradiation wavelength was 350 nm).

Synthesis. Chart S1 depicts the three phenanthrolines **1-3** investigated in the present study. Synthesis of compounds **2** and **3** has been published earlier by our group.[2] In Scheme S1, the preparation of **1** is described. Sonogashira coupling[3] of iodobenzene and 3,8-diethynyl-2,9-dimesityl-[1,10]-phenanthroline[2] in presence of Pd(0) as catalyst led to formation of **1**.

Scheme S1. Synthesis of **1**.



Procedure for the synthesis of 2,9-dimesityl-3,8-bis(phenylethynyl)-[1,10]-phenanthroline (1). Iodobenzene (0.93 g, 4.6 mmol), 3,8-diethynyl-2,9-dimesityl-[1,10]-phenanthroline (0.21 g, 0.45 mmol)[2], $Pd(PPh_3)_4$ (0.1 g, 0.09 mmol) were suspended in benzene (15.0 mL) and triethylamine (7.5 mL) under nitrogen. The reaction mixture was heated at 60 °C for 6 h and monitored by ESI-MS. It was then diluted with CH_2Cl_2 (50 mL) and washed with saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification *via* column chromatography with ethylacetate-hexane (10 : 90, silica gel) 259 mg of **1** (yield 93%) were afforded as a colourless solid. mp 252–254 °C. ^{1}H NMR ([D_2]Dichloromethane, 400 MHz): δ = 8.49 (s, 2H), 7.89 (s, 2H), 7.28-7.30 (m, 6H), 7.17 (dd, *J* = 7.4, 2.0 Hz, 4H), 7.00 (s, 4H), 2.37 (s, 6H), 2.05 ppm (s, 12H). ^{13}C NMR ([D_2]Dichloromethane, 100 MHz): δ =162.5, 145.1, 138.8, 137.9, 137.4, 136.3, 131.9, 129.0, 128.7, 128.2, 127.6, 126.8, 123.0, 120.3, 95.3, 87.1, 21.3, 20.0 ppm. IR (KBr): ν = 2951, 2917, 2855, 2360, 1614, 1404 cm^{-1}. MS (ESI): *m/z* (%) $[C_{46}H_{36}N_2 + H]^+$: Calcd. 617.3, found 617.4. Elemental analysis, calcd. (%) for $C_{46}H_{36}N_2$: C 89.58, H 5.88, N 4.54; found C 88.99, H 5.87, N 4.49.

[2] M. Schmittel, C. Michel and A. Wiegrefe, *Synthesis*, 2005, 367.
[3] M. Schmittel, V. Kalsani, P. Mal and J. W. Bats, *Inorg. Chem.*, 2006, **45,** 6370.

Figure S1. ^{1}H NMR spectrum of **1** ([D_2]Dichloromethane, 400 MHz).

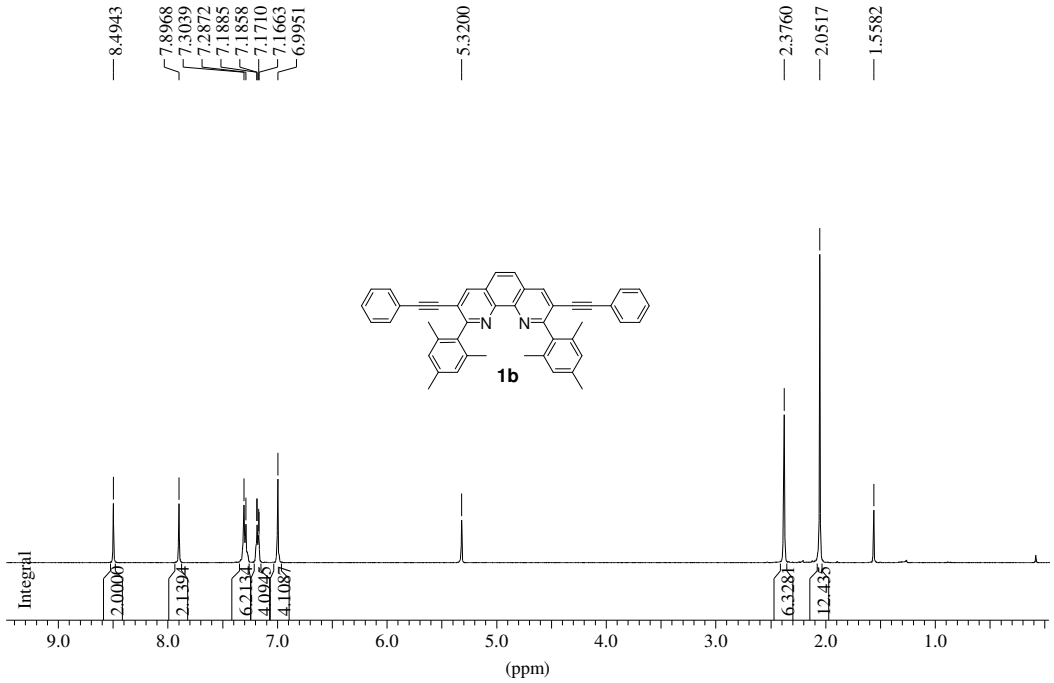


Figure S2. ^{13}C NMR spectrum of **1** ([D_2]Dichloromethane, 100 MHz).

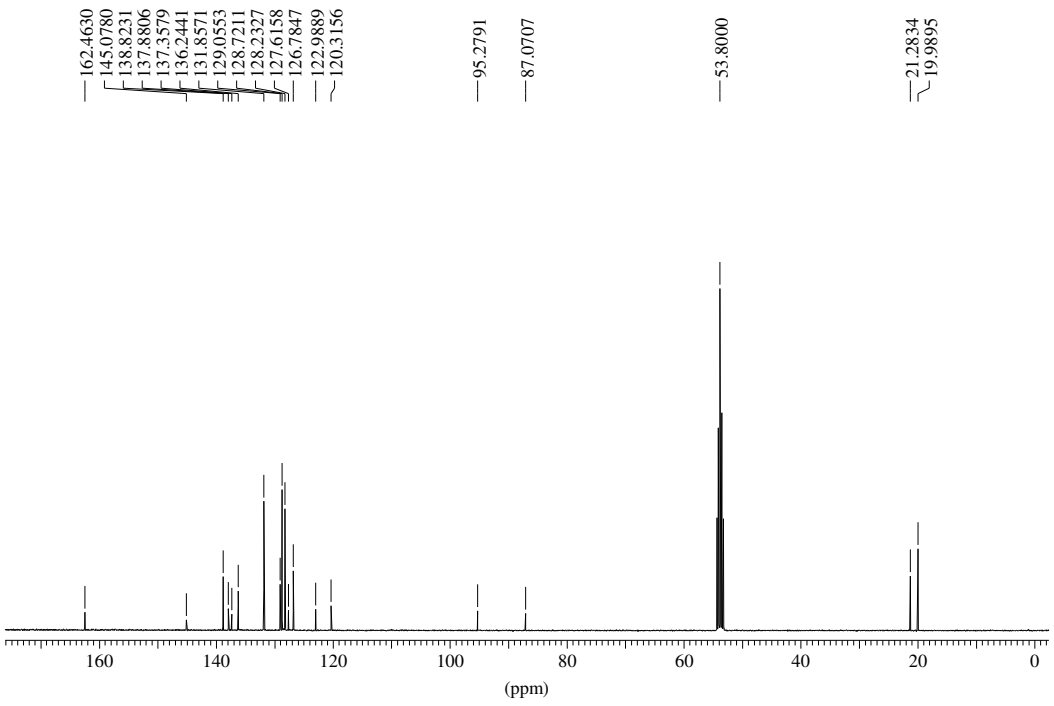
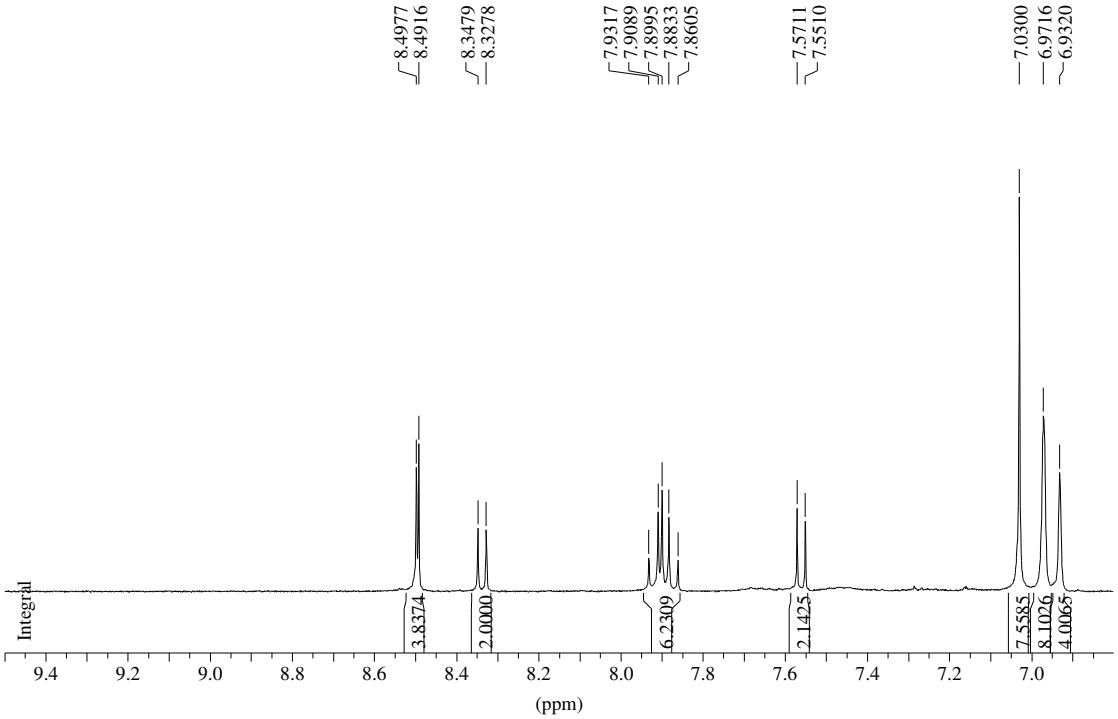


Figure S3. ^{1}H NMR spectra (400 MHz) of **3** (top) and **3** + methanesulfonic acid (bottom: 5.0 equivalents of methanesulfonic acid were used) in CD_2Cl_2-CD_3OD (4:1).

3



3 + H$^+$

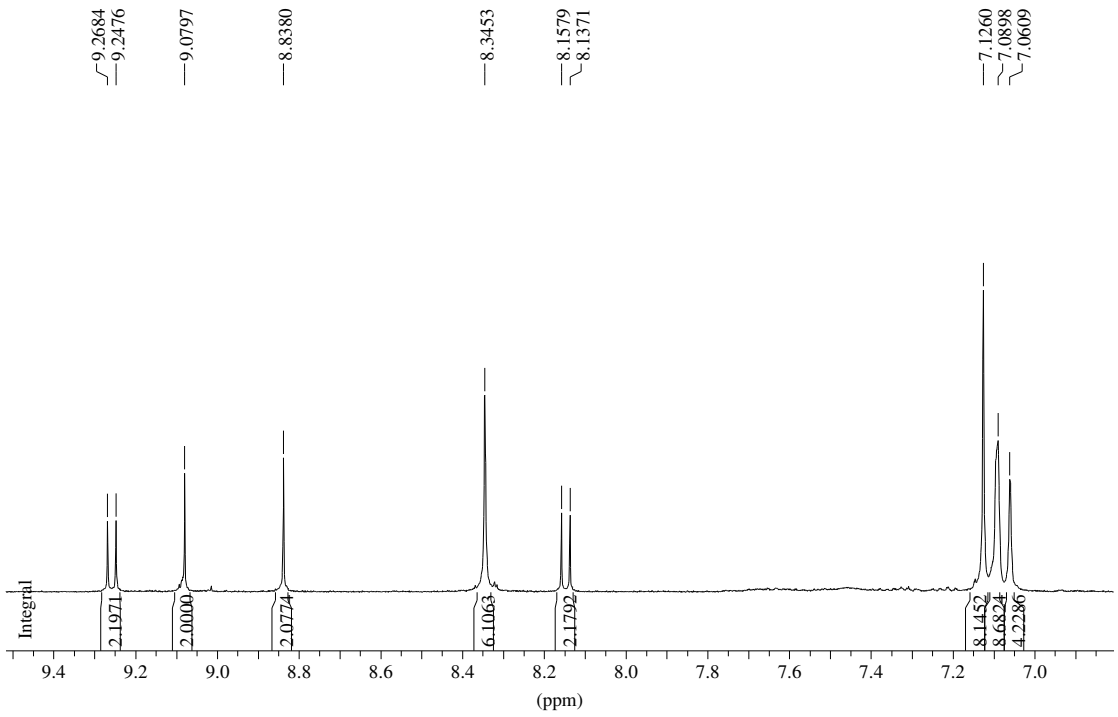


Figure S4. UV-Vis and luminescence spectra of **1** (1.0×10^{-5} M) upon progressive addition of methanesulfonic acid (1.0×10^{-3} M) in CH_2Cl_2-MeOH (4:1) at rt (a total of 2.0 equivalents of acid was added). Excitation wavelength: 308 nm.

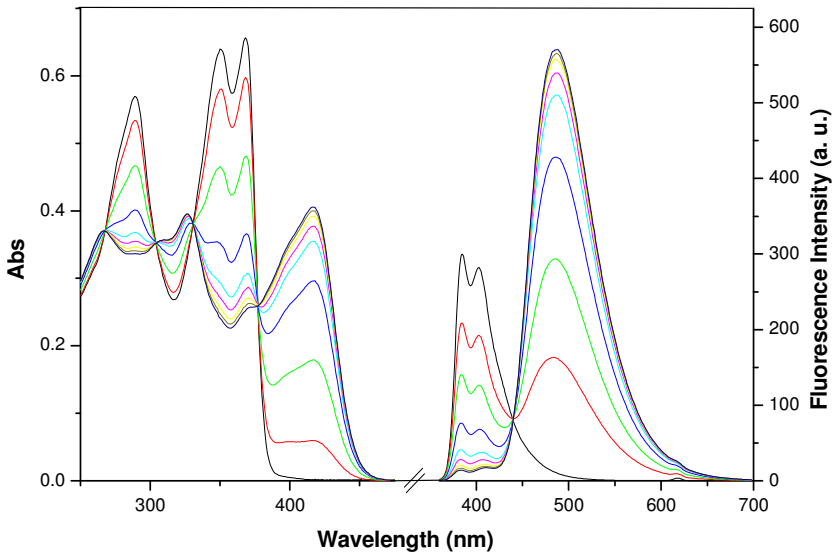


Figure S5. UV-Vis and luminescence spectra of **2** (1.0×10^{-5} M) upon progressive addition of methanesulfonic acid (1.0×10^{-3} M) in CH_2Cl_2-MeOH (4:1) at rt (a total of 3.0 equivalents of acid was added). Excitation wavelength: 275 nm.

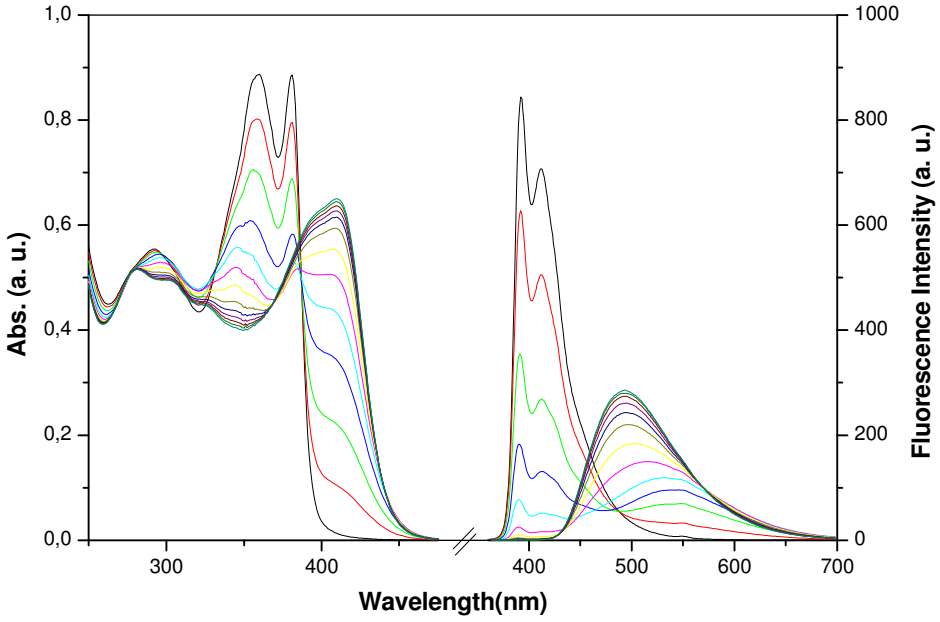


Figure S6. The speciation curves of **2** in presence of methanesulfonic acid.

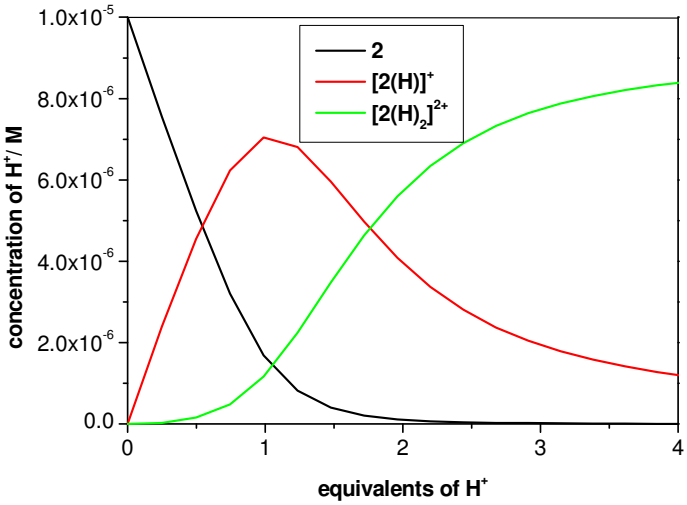


Figure S7. UV-Vis and luminescence spectra of **3** (1.0×10^{-5} M) upon progressive addition of methanesulfonic acid (1.0×10^{-3} M) in CH_2Cl_2-MeOH (4:1) at rt (a total of 4.0 equivalents of acid was added). Excitation wavelength: 330 nm.

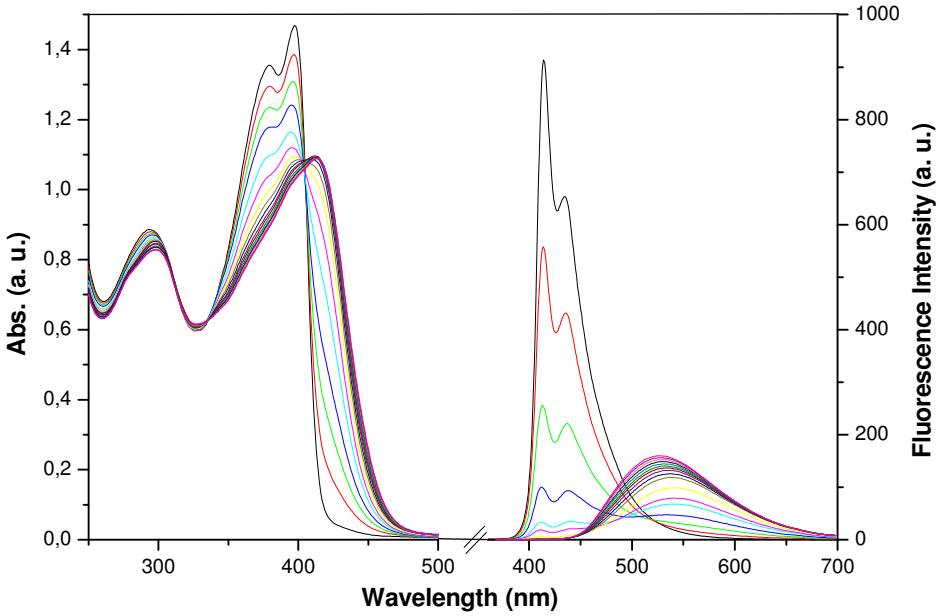


Figure S8. Change in the luminescence intensity of **3** (1.0×10^{-5} M) at 414 nm upon addition of methanesulfonic acid (1.0×10^{-3} M) in CH_2Cl_2-MeOH (4:1) at rt. Excitation wavelength: 330 nm.

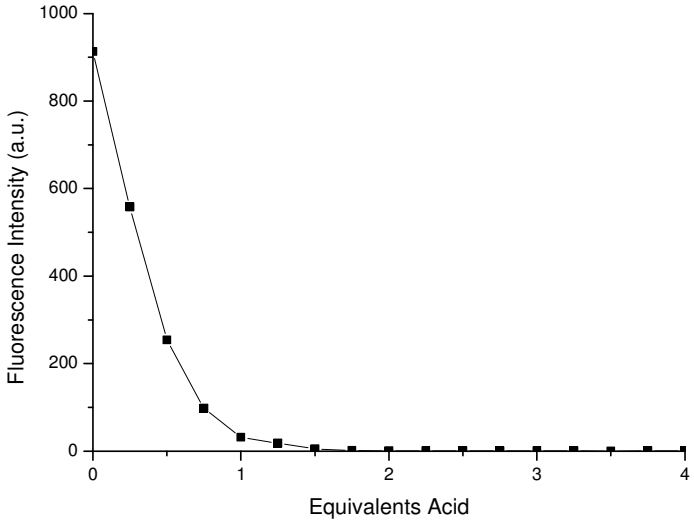


Figure S9. The speciation curves of **3** in presence of methanesulfonic acid.

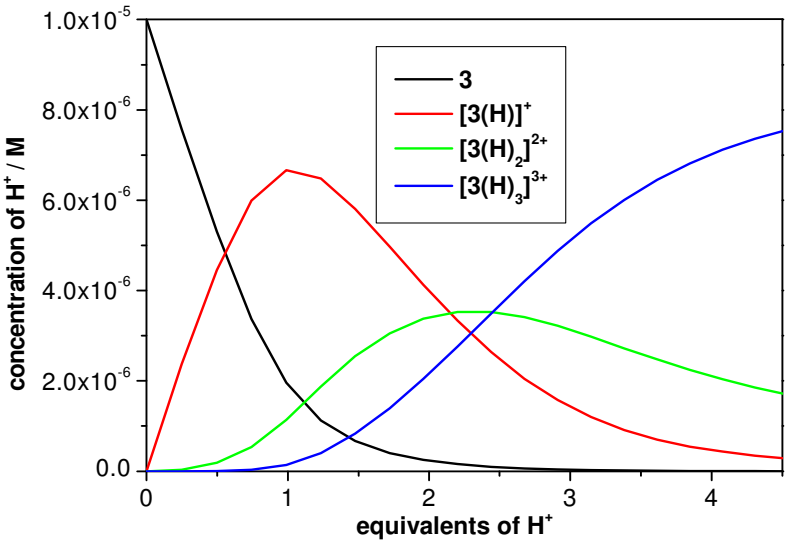


Figure S10. Luminescence spectra of **1** (2.0×10^{-5} M) upon progressive addition of methanesulfonic acid (2.0×10^{-3} M) and 1,4-benzoquinone (1×10^{-3} M) in CH_2Cl_2-MeOH (4:1) at rt. Excitation wavelength: 308 nm.

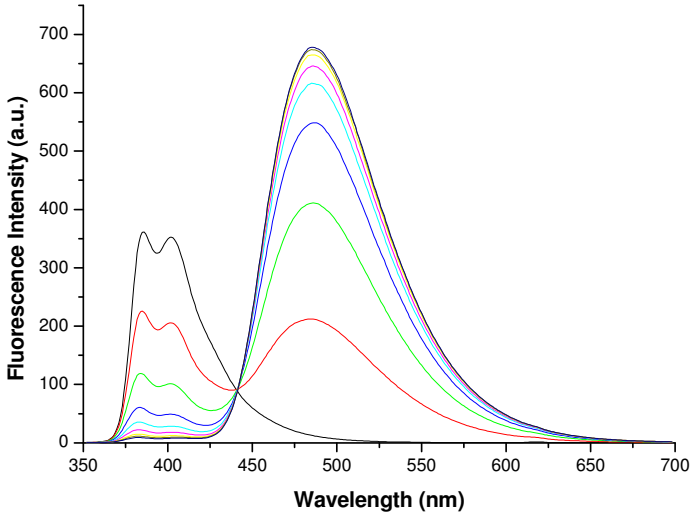


Figure S11. Luminescence spectra of a mixture of **3** (1.0×10^{-5} M) and 1,4-hydroquinone (3.0×10^{-5} M) upon progressive addition of tris(4-bromophenyl)aminium hexachloroantimonate (5.0×10^{-3} M) in CH_2Cl_2-MeOH (4:1) at rt. Excitation wavelength: 330 nm.

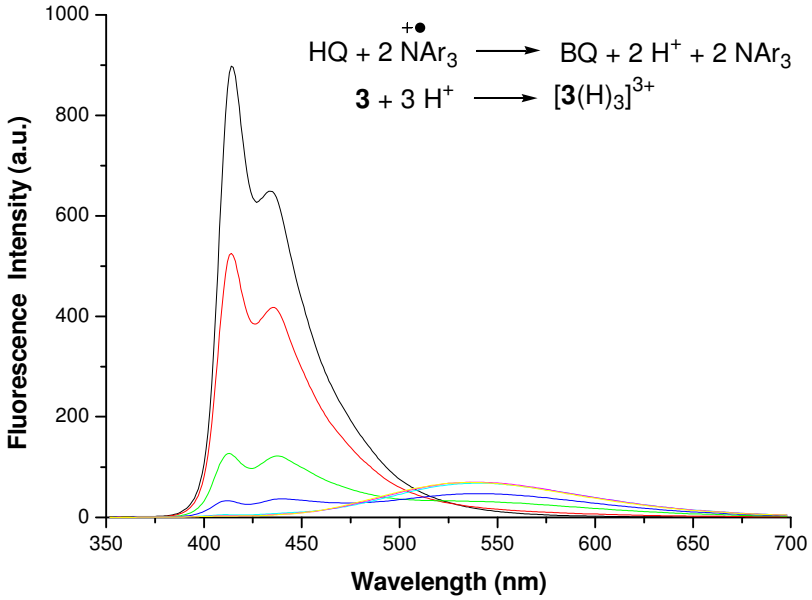
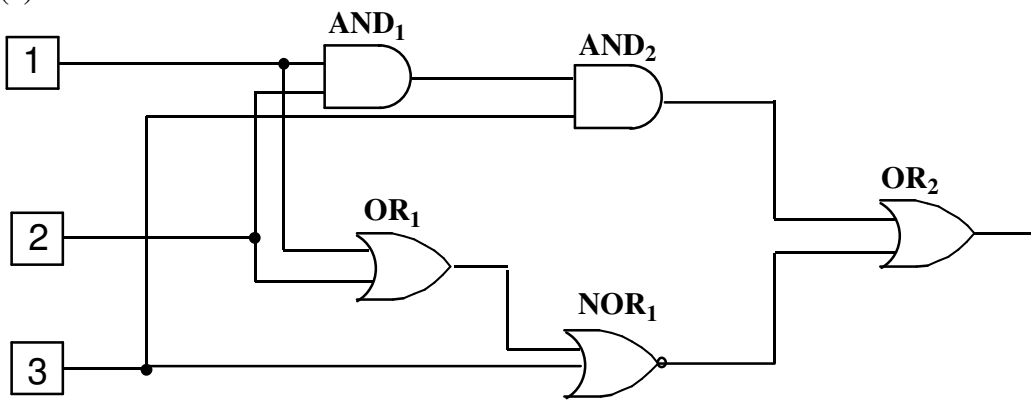


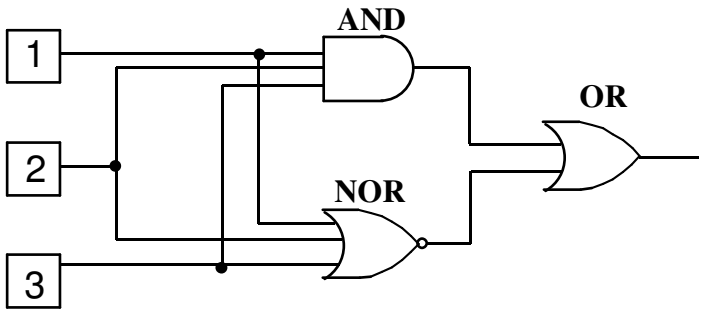
Figure S12. The schematic diagram of the 3-input AND – NOR – OR circuit and its operating truth table (a) on the basis of fundamental 2-input gates, and (b) on the basis of non-fundamental 3-input gates.

(a)



Input 1	Input 2	Input 3	AND_1	AND_2	OR_1	NOR_1	OR_2
0	0	0	0	0	0	1	1
0	0	1	0	0	0	0	0
0	1	0	0	0	1	0	0
0	1	1	0	0	1	0	0
1	0	0	0	0	1	0	0
1	0	1	0	0	1	0	0
1	1	0	1	0	1	0	0
1	1	1	1	1	1	0	1

(b)



Input 1	Input 2	Input 3	AND	NOR	OR
0	0	0	0	1	1
0	0	1	0	0	0
0	1	0	0	0	0
0	1	1	0	0	0
1	0	0	0	0	0
1	0	1	0	0	0
1	1	0	0	0	0
1	1	1	1	0	1

Table S1. Calculation of the intensity of each protonated species of **2** (normalised).

1 equiv. of acid added

Detected species	% (Calculated from speciation curve)	I_{em} [a] (a. u.)	$I_{em\text{-}norm.} = I_{em}$ / % (a. u.)	$I_{em\text{-}norm.}/I_{em}^{00}$ [b]
2	0.16	58 (λ = 389 nm)	362	1
$[\mathbf{2}(H)]^{+}$	0.70	83 (λ = 530 nm)	118	0.14
$[\mathbf{2}(H)_2]^{2+}$	0.13	30 (λ = 484 nm)	231	0.27

2 equiv. of acid added

Detected species	% (Calculated from speciation curve)	I_{em} [a] (a. u.)	$I_{em\text{-}norm.} = I_{em}$ / % (a. u.)	$I_{em\text{-}norm.}/I_{em}^{00}$ [b]
2	0.02	--	--	--
$[\mathbf{2}(H)]^{+}$	0.38	33 (λ = 530 nm)	87	0.10
$[\mathbf{2}(H)_2]^{2+}$	0.60	169 (λ = 484 nm)	282	0.33

3 equiv. of acid added

Detected species	% (Calculated from speciation curve)	I_{em} [a] (a. u.)	$I_{em\text{-}norm.} = I_{em}$ / % (a. u.)	$I_{em\text{-}norm.}/I_{em}^{00}$ [b]
2	0	--	--	--
$[\mathbf{2}(H)]^{+}$	0.18	20 (λ = 530 nm)	111	0.13
$[\mathbf{2}(H)_2]^{2+}$	0.80	242 (λ = 484 nm)	302	0.36

[a] Intensity data for each species after deconvolution, [b] I_{em}^{00} = 843 a. u. (λ = 392 nm)

Table S2. (a) XNOR logic operation of **2** with progressive addition of methanesulfonic acid (b) truth table of a molecular XNOR gate

(a)

entry	substrate	λ_{max}^{em} /nm	I_{em}/I_o [a]	output [b]
1	00	392	≡1.00	1
2	10/01	531	0.12±0.03	0
3	11	494	0.32±0.04	1

(b)

Input 1	Input 2	XNOR
0	0	1
0	1	0
1	0	0
1	1	1

Table S3. Calculation of the intensity of each protonated species of **3** (normalised).

1 equiv. of acid added

Detected species	% (Calculated from speciation curve)	I_{em} [a] (a. u.)	$I_{em\text{-}norm.} = I_{em}$ / % (a. u.)	$I_{em\text{-}norm.}/I_{em}^{000}$ [b]
3	0.20	32 (λ = 411 nm)	160	1
$[\mathbf{3}(H)]^{+}$	0.67	46 (λ = 534 nm)	69	0.076
$[\mathbf{3}(H)_2]^{2+}$	0.12	8 (λ = 636 nm)	67	0.073
$[\mathbf{3}(H)_3]^{3+}$	0.01	--	--	--

2 equiv. of acid added

Detected species	% (Calculated from speciation curve)	I_{em} [a] (a. u.)	$I_{em\text{-}norm.} = I_{em}$ / % (a. u.)	$I_{em\text{-}norm.}/I_{em}^{000}$ [b]
3	0.02	--	--	--
$[\mathbf{3}(H)]^{+}$	0.40	28 (λ = 534 nm)	70	0.077
$[\mathbf{3}(H)_2]^{2+}$	0.34	22 (λ = 635 nm)	65	0.071
$[\mathbf{3}(H)_3]^{3+}$	0.22	56 (λ = 518 nm)	254	(0.28) [c]

3 equiv. of acid added

Detected species	% (Calculated from speciation curve)	I_{em} [a] (a. u.)	$I_{em\text{-}norm.} = I_{em}$ / % (a. u.)	$I_{em\text{-}norm.}/I_{em}^{000}$ [b]
3	0	--	--	--
$[\mathbf{3}(H)]^{+}$	0.15	10 (λ = 535 nm)	67	0.073
$[\mathbf{3}(H)_2]^{2+}$	0.32	20 (λ = 634 nm)	63	0.069
$[\mathbf{3}(H)_3]^{3+}$	0.51	118 (λ = 517 nm)	231	0.25

4.0 equiv. of acid added

Detected species	% (Calculated from speciation curve)	I_{em} [a] (a. u.)	$I_{em\text{-}norm.} = I_{em}$ / % (a. u.)	$I_{em\text{-}norm.}/I_{em}^{000}$ [b]
3	0	--	--	--
$[\mathbf{3}(H)]^{+}$	0.05	3.4 (λ = 535 nm)	68	0.074
$[\mathbf{3}(H)_2]^{2+}$	0.22	14 (λ = 634 nm)	64	0.070
$[\mathbf{3}(H)_3]^{3+}$	0.72	141 (λ = 518 nm)	196	0.21

[a] Intensity data for each species after deconvolution, [b] I_{em}^{000} = 913 (λ = 414 nm), [c] This value was not used for the determination of the arithmetic mean value of $I_{em\text{-}norm.}/I_{em}^{000}$ of $[\mathbf{3}(H)_3]^{3+}$.