Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for:

Optically sensed, molecular shuttles driven by acid-base chemistry

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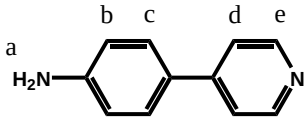
Synthesis of 4-Pyridyl-4-aniline

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (5.00 g, 2.28×10^{-2} mol), 4-bromopyridine hydrochloride (4.44 g, 2.28×10^{-2} mol) and sodium carbonate (12.10 g, 1.14×10^{-1} mol) were dissolved in DMF (200 mL) and H_2O (100 mL) and degassed with N_2(g) for 2 h. Tetrakis(triphyenylphosphine)palladium(0) (1.32 g, 1.14×10^{-4} mol) was added and the solution degassed for an additional 1 h. The reaction was refluxed for 24 h and subsequently cooled to room temperature. The DMF and H_2O were removed by rotary evaporation. The resulting residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (3 x 100 mL). The CH_2Cl_2 was dried with anhydrous $MgSO_4$, filtered and concentrated. The product precipitated from CH_2Cl_2 as a pale yellow powder. (1.15 g, 80%)



^{1}H NMR Spectroscopic Data ($CDCl_3$)

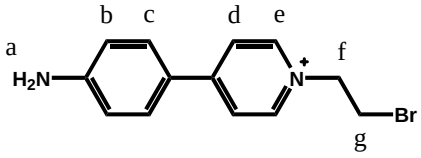
Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	3.88	br, s	2	--
b	6.76	d	2	$^3J_{bc} = 8.42$
c	7.49	d	2	$^3J_{cb} = 8.42$
d	7.44	d	2	$^3J_{de} = 6.08$
e	8.57	d	2	$^3J_{ed} = 6.08$

^{1}H NMR Spectroscopic Data (CD_3CN)

Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	4.43	br s	2	--
b	6.73	d	2	$^3J_{bc} = 8.43$
c	7.52	d	2	$^3J_{cb} = 8.43$
d	7.50	d	2	$^3J_{de} = 5.76$
e	8.50	d	2	$^3J_{ed} = 5.76$

Synthesis of 1[OTf]

4-Pyridyl-4-aniline (1.00 g, 5.88×10^{-3} mol) was refluxed in 1,2-dibromoethane (40 mL) and ethanol (20 mL) for 6 h. The precipitate that formed was collected by vacuum filtration. The precipitate was stirred in CH_2Cl_2 and filtered. This afforded a yellow solid as the bromide salt (0.921 g, 44%) The bromide salt was anion exchanged to the triflate salt by dissolving the solid in H_2O, warming the solution and adding sodium triflate, $[Na][CF_3SO_3]$. The solution was cooled and the yellow crystals were collected by vacuum filtration. (1.05 g, 96%)



^{1}H NMR Spectroscopic Data (D_2O, as Br salt)

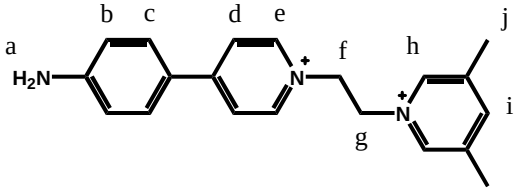
Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	--	--	2	--
b	6.81	d	2	$^3J_{bc} = 8.69$
c	7.71	d	2	$^3J_{cb} = 8.69$
d	8.03	d	2	$^3J_{de} = 6.86$
e	8.50	d	2	$^3J_{ed} = 6.86$
f	4.76	t	2	$^3J_{fg} = 5.70$
g	3.83	t	2	$^3J_{gf} = 5.70$

^{1}H NMR Spectroscopic Data (CD_3CN, as OTf salt)

Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	5.12	br s	2	--
b	6.79	d	2	$^3J_{bc} = 8.71$
c	7.78	d	2	$^3J_{cb} = 8.71$
d	8.08	d	2	$^3J_{de} = 6.89$
e	8.42	d	2	$^3J_{ed} = 6.89$
f	4.74	t	2	$^3J_{fg} = 5.88$
g	3.89	t	2	$^3J_{gf} = 5.88$

Synthesis of 2[OTf]$_2$

Compound **1**[OTf] (0.635 g, 1.49×10^{-3} mol) and 3,5-lutidine (0.239 g, 2.23×10^{-3} mol) were dissolved in acetonitrile (25 mL) and refluxed for 24 hours. The precipitate that formed was isolated by vacuum filtration and washed with CH_2Cl_2. This yielded the product as a yellow solid as the bromide salt (0.150 g, 21%) The bromide salt was anion exchanged to the triflate salt by dissolving the solid in H_2O, warming the solution and adding NaOTf. The solution was cooled and the yellow crystals collected by vacuum filtration.



^{1}H NMR Spectroscopic Data (D_2O, as Br salt)

Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	--	--	2	--
b	6.80	d	2	$^3J_{bc} = 8.76$
c	7.71	d	2	$^3J_{cb} = 8.76$
d	8.01	d	2	$^3J_{de} = 7.02$

e	8.27	d	2	$^3J_{ed}$ = 7.02
f	5.04	t	2	$^3J_{fg}$ = 5.72
g	4.98	t	2	$^3J_{gf}$ = 5.72
h	8.31	s	2	--
i	8.18	s	1	--
j	2.30	s	6	--

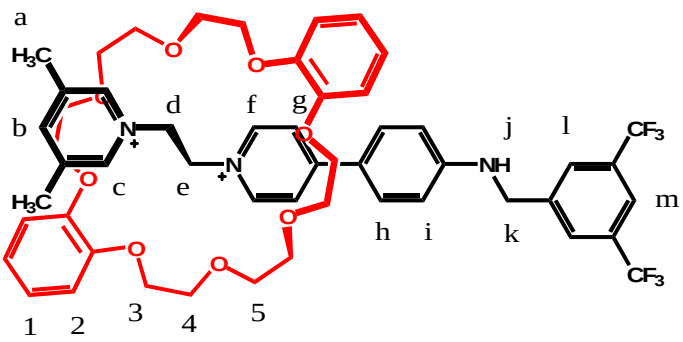
^{1}H NMR Spectroscopic Data (CD_3CN, as OTf salt)

Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	5.18	br s	2	--
b	6.80	d	2	$^3J_{bc}$ = 8.80
c	7.79	d	2	$^3J_{cb}$ = 8.80
d	8.06	d	2	$^3J_{de}$ = 7.12
e	8.30	d	2	$^3J_{ed}$ = 7.12
f	4.96	m	2	--
g	4.90	m	2	--
h	8.36	s	2	--
i	8.22	s	1	--
j	2.45	s	6	--

Synthesis of 3[OTf]$_3$

Compound **2**[Br]$_2$ (0.200 g, 4.30 × 10^{-4} mol), **DB24C8** (0.964 g, 2.14 × 10^{-3} mol) and 3,5-bis(trifluoromethyl)benzylbromide (0.066 g, 2.15 × 10^{-4} mol) were dissolved in a two layer CH_3NO_2 (10 mL) and H_2O (5 mL) solution to which NaOTf (0.150 g, 8.60 × 10^{-4} mol) was added and this mixture stirred at room temperature for 7 days. The CH_3NO_2 layer was separated from the H_2O layer, washed several times with water and dried with anhydrous $MgSO_4$. The CH_3NO_2 was evaporated and the residue washed several times with toluene to get rid of excess 3,5-bis(trifluoromethyl)benzylbromide and **DB24C8**. The rotaxane was further purified by column chromatography on silica get using 7:2:1 MeOH: 2M NH_4Cl: $MeNO_2$ as the eluent. The

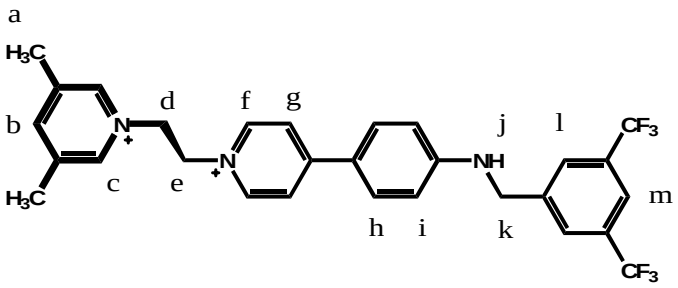
isolated solid was dissolved in CH_3NO_2 and NaOTf added. The resulting solid was then washed with water numerous times. The product was isolated as a yellow solid. (R_f = 0.82, 0.070 g, 26%), ESI-MS: *m/z* [**3**-OTf]$^+$ calc. 1128.3721, found 1128.3763. The stoppered axle **4**[OTf]$_3$ was also isolated from the column. It was dissolved in CH_3NO_2 and NaOTf added. The resulting solid was then repeatedly washed with water. The product was isolated as a yellow solid. (R_f = 0.64, 0.020 g, 7%), ESI-MS: *m/z* [**4**-OTf]$^+$ calc. 680.1624, found 680.1634.



H NMR Spectroscopic Data (CD_3CN)

Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	2.15	s	6	--
b	7.59	s	1	--
c	8.55	s	2	--
d	5.33	m	2	--
e	5.26	m	2	--
f	8.80	d	2	$^3J_{fg}$ = 7.01
g	7.84	d	2	$^3J_{gf}$ = 7.01
h	7.58	d	2	$^3J_{hi}$ = 8.72
i	6.71	d	2	$^3J_{ih}$ = 8.72
j	6.13	t	1	--
k	4.63	d	2	--
l	7.97	s	2	--
m	7.93	s	1	--
1-2	6.71	m	4	--

3-5	3.85-4.03	m	24	--



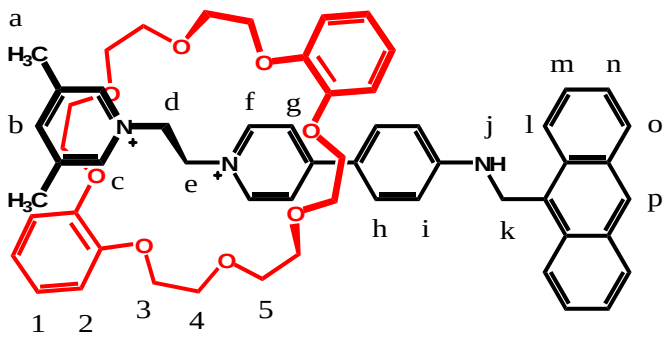
^{1}H NMR Spectroscopic Data (CD_3CN)

Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	2.44	s	6	--
b	8.21	s	1	--
c	8.37	s	2	--
d	4.95	t	2	$^3J_{de}$ = 5.46
e	4.91	t	2	$^3J_{ed}$ = 5.46
f	8.32	d	2	$^3J_{fg}$ = 7.04
g	8.06	d	2	$^3J_{gf}$ = 7.04
h	7.81	d	2	$^3J_{hi}$ = 8.86
i	6.78	d	2	$^3J_{ih}$ = 8.86
j	6.21	br s	1	--
k	4.62	d	2	$^3J_{kj}$ = 5.21
l	7.95	s	2	--
m	7.92	s	1	--

Synthesis of 5[OTf]$_3$

Compound **2**[Br]$_2$ (0.240 g, 5.16 × 10^{-4} mol), **DB24C8** (1.16 g, 2.58 × 10^{-3} mol) and 9-bromomethylanthracene (0.070 g, 2.58 × 10^{-4} mol) were dissolved in a two layer CH_3NO_2 (10 mL) and H_2O (5 mL) solution to which NaOTf (0.300 g, 1.74 × 10^{-3} mol) was added and stirred at room temperature for 7 days. The nitromethane layer was separated from the water layer, washed several times with water and dried with anhydrous $MgSO_4$. The nitromethane was

evaporated and the residue washed several times with toluene to get rid of excess 9-bromomethylanthracene and **DB24C8**. The rotaxane was further purified by column chromatography on silica get using 7:2:1 MeOH: 2M NH_4Cl: $MeNO_2$ as the eluent. The isolated solid was dissolved in CH_3NO_2 and NaOTf added. The resulting solid was then washed with water numerous times. The product was isolated as a yellow solid. (R_f =0.81, 0.085 g, 27%), ESI-MS: *m/z* [**5**-OTf]$^+$ calc. 1092.4286, found 1092.4282.



^{1}H NMR Spectroscopic Data (CD_3CN)

Proton	δ (ppm)	Multiplicity	# Protons	*J* (Hz)
a	2.16	s	6	--
b	7.59	s	1	--
c	8.57	s	2	--
d	5.36	m	2	--
e	5.28	m	2	--
f	8.80	d	2	$^3J_{fg}$ = 6.94
g	7.88	d	2	$^3J_{gf}$ = 6.94
h	7.69	d	2	$^3J_{hi}$ = 8.64
i	6.95	d	2	$^3J_{ih}$ = 8.64
j	5.59	t	1	$^3J_{jk}$ = 4.07
k	5.33	br s	2	$^3J_{kj}$ = 4.07
l	8.14	d	2	$^3J_{lm}$ = 8.51
m	7.61	ddd	2	$^3J_{ml}$ = 8.51. $^3J_{mn}$ = 6.97, $^4J_{mo}$ = 1.09

n	7.56	dd	2	$^3J_{no}$ = 8.01, $^3J_{nm}$ = 6.97
o	8.33	d	2	$^3J_{on}$ = 8.01
p	8.63	s	1	--
1-2	6.76	br s	8	--
3-5	3.79-4.06	m	24	--