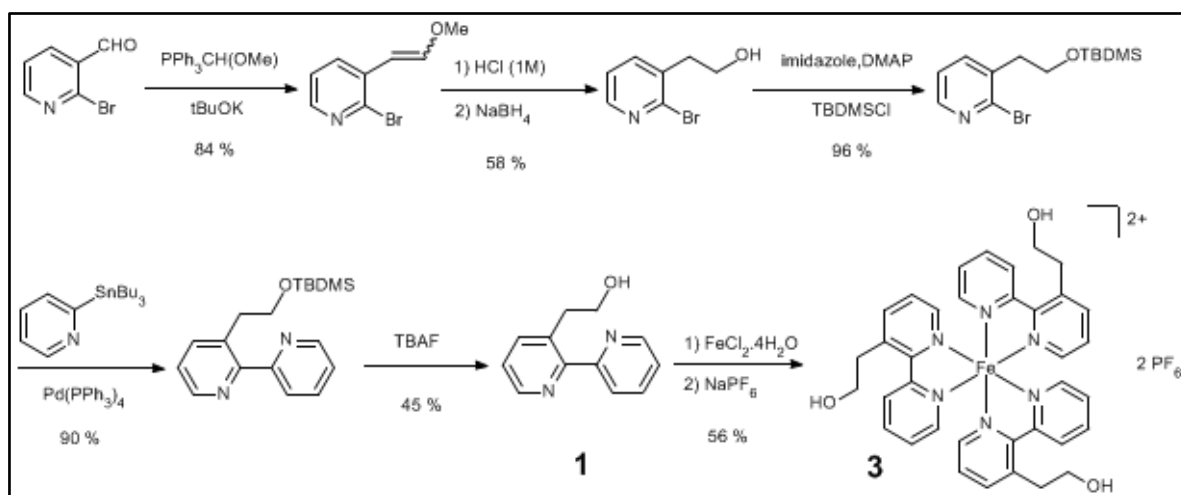


## Supplementary Information

### Chromogenic detection of Sarin by discolouring decomplexation of a metal coordination complex.

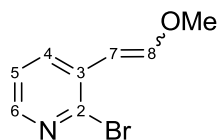
Lucie ORDRONNEAU, Alexandre CARELLA, Miroslav POHANKA and Jean-Pierre SIMONATO

#### Chemical synthesis



#### General Experimental Details

All reactions were performed using standard Schlenk techniques under inert atmosphere of dry argon. Solvents and chemicals were purchased from Sigma-Aldrich and used as received. Proton and carbon nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra were recorded in deuterated solvents on Bruker Avance DMX 200 (200 MHz) or Bruker Avance-300 (300 MHz) spectrometers at 298 K. Chemical shifts are reported in ppm and were determined by reference to residual  $^1\text{H}$  and  $^{13}\text{C}$  solvent signals. UV-vis spectra were recorded on a Varian Cary 5000 photospectrometer. Column chromatography was performed on silica gel Geduran® 60 (0.063-0.200 mm) from Merck.

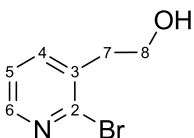


Molecule A

A 1.0 M of potassium *tert*-butoxide solution in THF (10 mL, 10 mmol) was added dropwise to a solution of (methoxymethyl)(triphenyl)phosphonium chloride (3.13 g, 9.14 mmol) in dry THF (30 mL) at 0°C under an atmosphere of argon. After stirring for 40 min at this temperature, a solution of 2-bromo-3-pyridinecarboxaldehyde (1 g, 5.38 mmol) in dry THF (10 mL) was added slowly. The resulting solution was stirred 25 min at 0°C, then at room temperature for 2 hours.

The reaction was quenched by addition of water and then the product was extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtrated and concentrated. The crude product was purified by column chromatography on silica gel using pentane/ethyl acetate (90:10) as eluant to give a mixture of olefin isomers (966 mg, 84%).

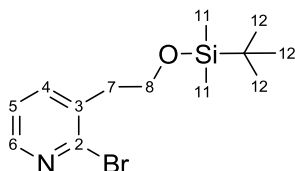
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ (ppm) 3.75 (s, 3H, OCH<sub>3</sub><sup>trans</sup>), 3.81 (s, 3H, OCH<sub>3</sub><sup>cis</sup>), 5.56 (d, 1H, 7.1 Hz, C=H<sup>cis</sup>), 5.99 (d, 1H, 12.9 Hz, C=H<sup>trans</sup>), 6.34 (d, 1H, 7.1 Hz, C=H<sup>cis</sup>), 6.99 (d, 1H, 12.9 Hz, C=H<sup>trans</sup>), 7.16 (dd, 1H, 7.7 Hz, 4.7 Hz, H<sup>5-trans</sup>), 7.19 (dd, 1H, 8 Hz, 4.8 Hz, H<sup>5-cis</sup>), 7.59 (dd, 1H, 7.8 Hz, 2 Hz, H<sup>4-trans</sup>), 8.11 (dd, 1H, 4.8 Hz, 1.8 Hz, H<sup>4-cis</sup>), 8.15 (dd, 1H, 4.6 Hz, 1.8 Hz, H<sup>6-cis</sup>), 8.31 (dd, 1H, 7.8 Hz, 1.8 Hz, H<sup>6-trans</sup>).



Molecule B

Compound **A** (746 mg, 3.48 mmol) was dissolved in dry THF (10 mL) under argon atmosphere, and a 1 M solution of hydrogen chloride in water (12 mL) was added. The mixture was heated at reflux for 3 hours. The reaction was cooled to room temperature and the product was extracted by ethyl acetate (2 times). The combined organic layers were washed with saturated NaHCO<sub>3</sub> solution and brine, dried over MgSO<sub>4</sub>, filtrated and concentrated. The light yellow oil was dissolved in dry methanol (15 mL) and cooled to 0°C, then the sodium borohydride (149.5 mg, 3.95 mmol) was added and the reaction stirred at this temperature for 45 min. The mixture was quenched by the addition of saturated ammonium chloride solution, the methanol was removed by rotary evaporation, then the remaining aqueous solution was extracted 3 times with ethyl acetate. The combined organic layers were dried over MgSO<sub>4</sub>, filtrated and concentrated. The crude product was purified by column chromatography on silica gel using pentane/ethyl acetate (1:1) as eluant to give a colourless oil (411 mg, 58 %).

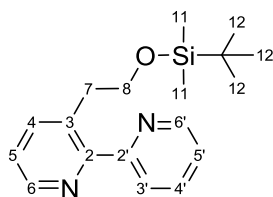
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 1.50 (t, 1H, 5.2 Hz, OH), 3.00 (t, 2H, 6.3 Hz,  $\text{CH}_2^7$ ), 3.94 (q, 2H, 6.4 Hz,  $\text{CH}_2^8$ ), 7.21 (m, 1H,  $\text{H}^5$ ), 7.61 (dd, 1H, 7.6 Hz, 2.2 Hz,  $\text{H}^4$ ), 8.25 (dd, 1H, 4.6 Hz, 2.0 Hz,  $\text{H}^6$ ).



Molecule C

Compound **B** (203 mg, 1.0 mmol), , was dissolved in dry methylene chloride (10 mL) under argon atmosphere, then, imidazole (11 mg, 1.63 mmol), dimethylaminopyridine (13 mg, 0.11 mmol) and *tert*-butyldimethylchlorosilane (183 mg, 1.21 mmol) was added. The mixture was stirred at room temperature overnight and then quenched by addition of water. The phases were separated and the organic layer was extracted with methylene chloride twice. The combined organic layers were dried over  $\text{MgSO}_4$ , filtrated and concentrated. The crude product was purified by column chromatography on silica gel using methylene chloride/methanol (96:4) as eluant to give a colourless oil (303 mg, 96 %).

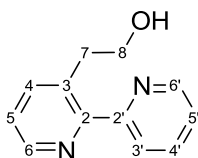
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -0.05 (s, 6H,  $\text{CH}_3^{11}$ ), 0.84 (s, 9H,  $\text{CH}_3^{12}$ ), 2.94 (t, 2H, 6.4 Hz,  $\text{CH}_2^7$ ), 3.86 (t, 2H, 6.6 Hz,  $\text{CH}_2^8$ ), 7.19 (dd, 1H, 7.4 Hz, 4.6 Hz,  $\text{H}^5$ ), 7.57 (dd, 1H, 7.4 Hz, 1.8 Hz,  $\text{H}^4$ ), 8.23 (dd, 1H, 4.6 Hz, 2.0 Hz,  $\text{H}^6$ ).



Molecule D

In a solution of compound **C** (78 mg, 0.25 mmol) in dry toluene, under argon atmosphere, were added 2-(tributylstannyl)pyridine (0.12 mL, 0.31 mmol) and tetrakis(-triphenyl)phosphine) palladium (50 mg, 0.043 mmol) and the mixture was stirred at reflux overnight. The reaction was cooled to room temperature and water was added. The product was extracted twice with methylene chloride. The combined organic layers were dried over  $\text{MgSO}_4$ , filtrated and concentrated. The crude product was purified by column chromatography on silica gel using methylene chloride/methanol (96:4) to give a colorless oil (70 mg, 90 %).

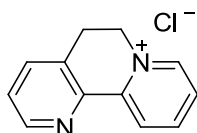
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -0.09 (s, 6H,  $\text{CH}_3^{11}$ ), 0.82 (s, 9H,  $\text{CH}_3^{12}$ ), 3.13 (t, 2H, 6.8 Hz,  $\text{CH}_2^7$ ), 3.78 (t, 2H, 7.2 Hz,  $\text{CH}_2^8$ ), 7.31 (m, 1H), 7.49 (m, 2H), 7.67 (m, 1H), 7.83 (d, 1H, 3.6 Hz), 8.57 (dd, 1H, 4.8 Hz, 1.6 Hz), 8.67 (d, 1H, 4.8 Hz,  $\text{H}^6$ ).



### Molecule 1

In a solution of compound **D** (70 mg, 22 mmol) in dry THF, under argon atmosphere, was added tetrabutylammonium fluoride (1M in THF, 0.65 mL, 0.65 mmol). The mixture was stirred for 2 hours at room temperature and water was added. The compound was extracted with methylene chloride (2 times), and the combined organic layers were dried over  $\text{MgSO}_4$ , filtrated and concentrated. The crude product was purified by column chromatography on silica gel using methylene chloride/methanol (95:5) to give a colourless oil (20 mg, 45 %).

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) 2.99 (t, 2H, 5.7 Hz,  $\text{CH}_2^7$ ), 3.98 (t, 2H, 5.7 Hz,  $\text{CH}_2^8$ ), 7.35 (dd, 1H, 7.8 Hz, 4.8 Hz,  $\text{H}^5$ ), 7.39 (ddd, 1H, 7.2 Hz, 4.8 Hz, 1.2 Hz,  $\text{H}^4$  ou  $\text{H}^5$ ), 7.74 (dd, 1H, 7.8 Hz, 1.5 Hz,  $\text{H}^4$ ), 7.74 (td, 1H, 7.2 Hz, 1.8 Hz,  $\text{H}^4$  ou  $\text{H}^5$ ), 7.99 (dt, 1H, 8.1 Hz, 0.9 Hz,  $\text{H}^3$  ou  $\text{H}^6$ ), 8.56 (dd, 1H, 4.8 Hz, 1.5 Hz,  $\text{H}^6$ ), 8.59 (m, 1H,  $\text{H}^3$  ou  $\text{H}^6$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm) 3.00 (t, 2H, 6.0 Hz), 3.83 (t, 2H, 6.0 Hz), 5.32 (m, 1H, OH), 7.41 (m, 2H), 7.80 (dd, 1H, 7.8 Hz, 1.8 Hz), 7.94 (m, 2H), 8.54 (dd, 1H, 4.5 Hz, 1.5 Hz), 8.60 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) 34.64 ( $\text{CH}_2^7$ ), 63.75 ( $\text{CH}_2^8$ ), 123.14, 123.69, 125.30, 134.94, 137.66, 138.95, 146.76, 147.22, 155.70, 157.57  
ESI MS ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ )  $m/z$  (a.m.u) calcd for  $(\text{M}+\text{H})^+$  [ $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}$ ] $^+$ : 201.10; found: 201.1



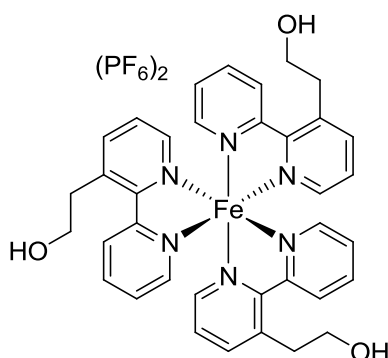
### Molecule 2

Thionyl chloride (1.5 mL) was added to compound **1** (0.03 mmol). The mixture was stirred at room temperature for one hour, and then the yellow solution was concentrated to give compound **2**.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm) 3.40 (t, 2H, 6.6 Hz), 4.82 (t, 2H, 6.9 Hz), 7.61 (m, 1H), 7.90 (d, 1H, 7.8 Hz), 7.98 (m, 1H), 8.58 (m, 1H), 8.73 (m, 2H), 8.88 (d, 1H, 7.8 Hz).  $^{13}\text{C}$  NMR (75 MHz,

CD<sub>3</sub>CN)  $\delta$  (ppm) 25.70 (C-CH<sub>2</sub>-CH<sub>2</sub>-N), 55.36 (C-CH<sub>2</sub>-CH<sub>2</sub>-N), 125.82, 128.02, 128.65, 132.91, 138.05, 144.34, 145.96, 147.32, 150.73

ESI MS (MeOH) m/z (a.m.u) calcd for (M-Cl)<sup>+</sup> [C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>]<sup>+</sup>: 183.2; found: 183.1



### Coordination complex 3

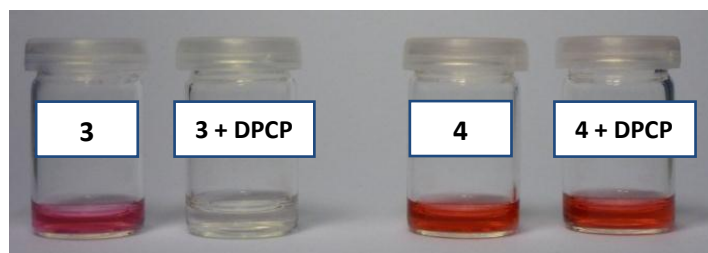
In a solution of compound **1** (50 mg, 0.25 mmol) in degassed ethylene dichloride, under argon atmosphere, was added iron chloride tetrahydrate (16.5 mg, 0.08 mmol) and the mixture was stirred under reflux overnight. The reaction was cooled to room temperature and the solvent was removed under reduce pressure. Then sodium hexafluorophosphate (150 mg) was added in a methylene chloride/acetonitrile mixture and stirred overnight at room temperature. After addition of water, the compound was extracted twice with methylene chloride, and the combined organic layers were dried over MgSO<sub>4</sub>, filtrated and concentrated. The crude product was washed with diethyl ether to give a pink-red powder (48 mg, 56 %) (mixture of isomers).

<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$  (ppm) 3.03 (m, 3H), 3.41 (m, 3H), 3.90 (t, 3H, 6.0 Hz), 3.98 (t, 3H, 6.3 Hz) 7.26 (m, 4H), 7.41 (m, 2H), 7.57 (m, 3H), 7.99 (m, 6H), 8.17 (m, 2H), 8.62 (m, 4H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN)  $\delta$  (ppm) 36.54, 60.63, 125.83, 126.32, 127.57, 137.95, 138.93, 141.96, 152.24, 154.53, 157.86, 160.09 (according to the presence of isomers, signals are split)

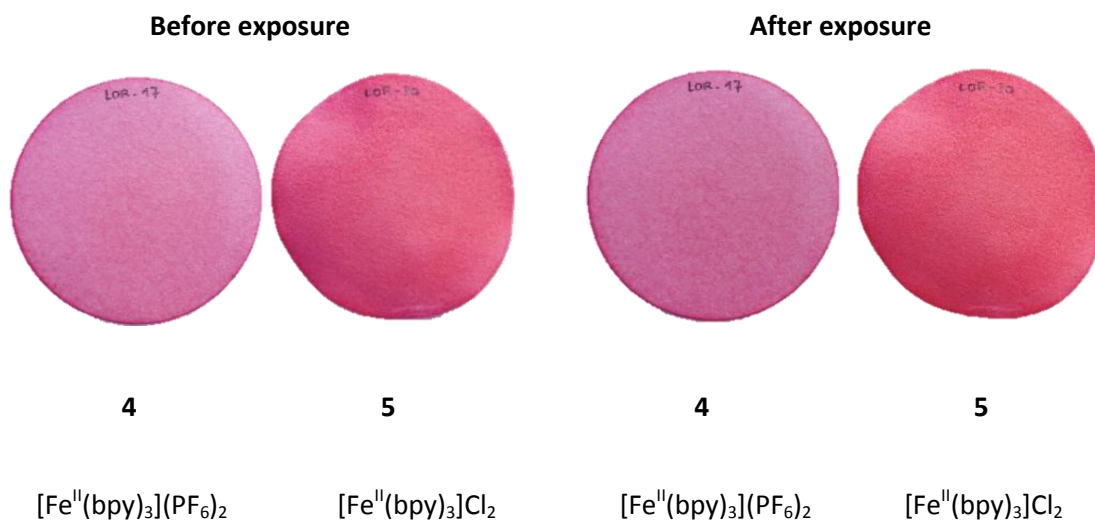
ESI MS (CH<sub>3</sub>CN) m/z (a.m.u) calcd for (M-2PF<sub>6</sub>) [C<sub>36</sub>H<sub>36</sub>FeN<sub>6</sub>O<sub>3</sub>]<sup>2+</sup>: 328.11; found: 328.2

UV-vis in CH<sub>3</sub>CN:  $\lambda_{\max}$  = 303 nm ( $\epsilon$  = 53195 L. mol<sup>-1</sup>. cm<sup>-1</sup>),  $\lambda_{\max}$  = 361 nm ( $\epsilon$  = 6657 L. mol<sup>-1</sup>. cm<sup>-1</sup>),  $\lambda_{\max}$  = 529 nm ( $\epsilon$  = 7887 L. mol<sup>-1</sup>. cm<sup>-1</sup>).

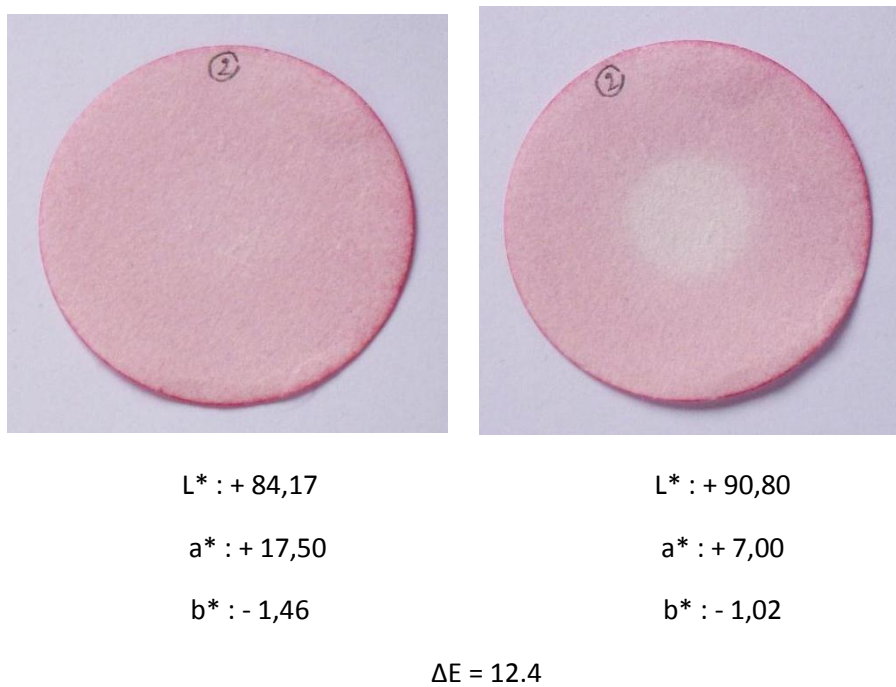
UV-vis in CH<sub>2</sub>Cl<sub>2</sub>:  $\lambda_{\max}$  = 304 nm ( $\epsilon$  = 20112 L. mol<sup>-1</sup>. cm<sup>-1</sup>),  $\lambda_{\max}$  = 364 nm ( $\epsilon$  = 2506 L. mol<sup>-1</sup>. cm<sup>-1</sup>),  $\lambda_{\max}$  = 531 nm ( $\epsilon$  = 2765 L. mol<sup>-1</sup>. cm<sup>-1</sup>).



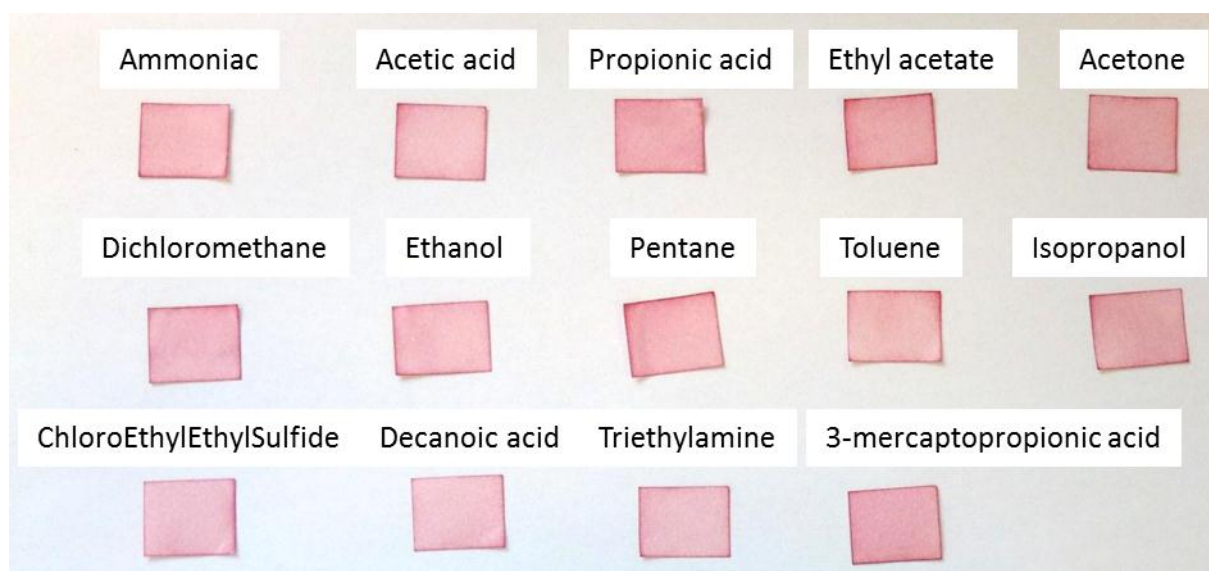
**Figure S1.** Effect of DPCP (100  $\mu$ L) addition to 0.3 mM  $\text{CH}_3\text{CN}$  solutions of coordination complexes **3**  $[\text{Fe}^{\text{II}}(\mathbf{1})_3](\text{PF}_6)_2$  and **4**  $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$



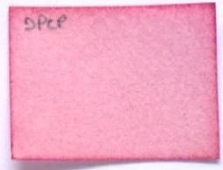
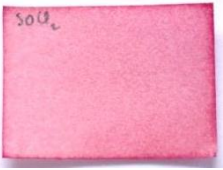
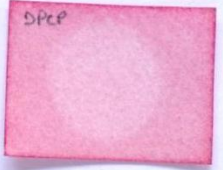
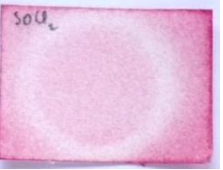
**Figure S2.** Reference complexes exposed to DPCP vapours



**Figure S3.** Paper with complex **3** exposed for 10 min to DPCP vapours. Values below pictures indicate color coordinates in according to the CIE L\*a\*b\* color space.



**Figure S4a.** Papers soaked with complex **3** exposed to various analytes at their vapour pressures at room temperature.

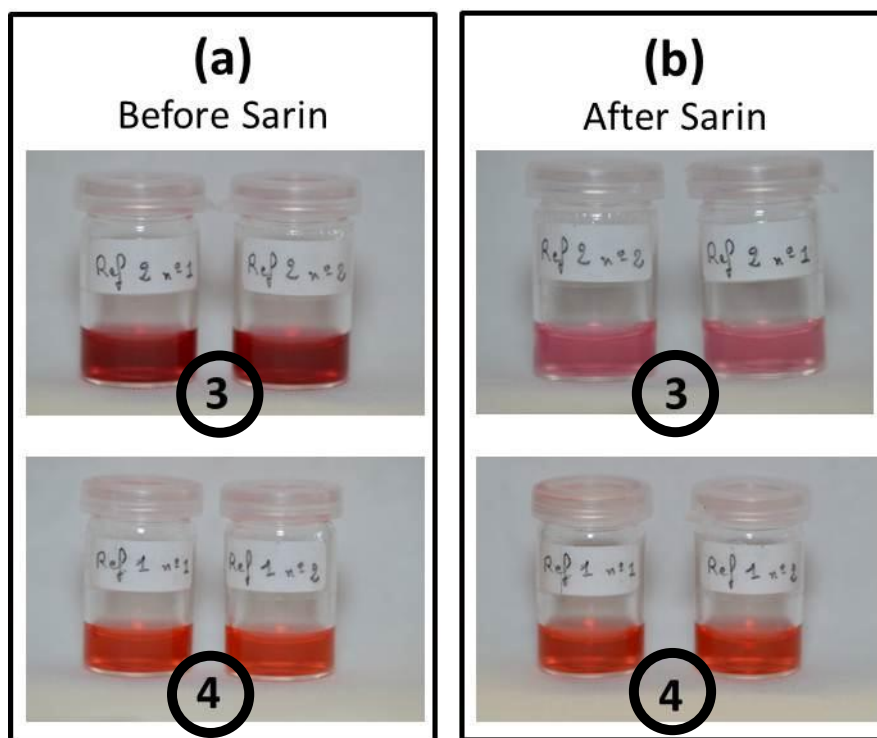
Before exposure		After vapor exposure (3 min)	
		DPCP	SOCl <sub>2</sub>
			
L* : +75.62 a* : +28.67 b* : -0.70	L* : +70.60 a* : +33.85 b* : +0.45	L* : +81.07 a* : +21.56 b* : -1.30	L* : +83.85 a* : +16.36 b* : -0.70

**Figure S4b.** Papers soaked with complex **3** exposed to DPCP and SOCl<sub>2</sub> at their vapour pressures at room temperature.

As explained by Ajami et al. (see Reference 8), molecular systems described so far for OP detection do not incorporate any molecular recognition – any acid chloride, acylating agent or even sulfonating agent would yield the same result – so they are not specific to OP's. However, acid chlorides and sulfonyl halides are also unhealthy things to have in the breathable atmosphere, so their sensing and destruction are not without merit.

Moreover, concerning this experiment with SOCl<sub>2</sub>, it must be taken into account that vapour pressure of thionyl chloride (110 mmHg at 26 °C) is significantly higher than the vapour pressure of DPCP.





**Figure S5.** Images of 0.5 mM solutions of **3**  $[\text{Fe}^{\text{II}}(\mathbf{1})_3](\text{PF}_6)_2$  and **4**  $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$  in  $\text{CH}_3\text{CN}$ , before (a) and after (b) Sarin addition. Each experiment was realized twice (2 vials).