

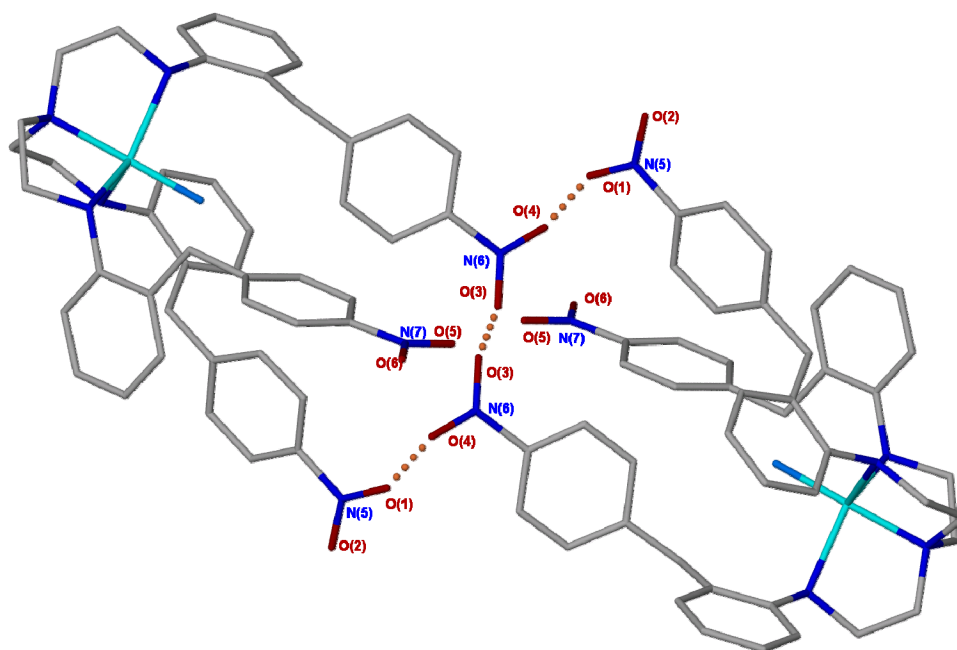
**Supplementary Information for:**

**Stabilisation of a very short Cu-F bond within the protected cavity of a copper(II)  
compound from a tris(2-aminoethyl)amine derivative**

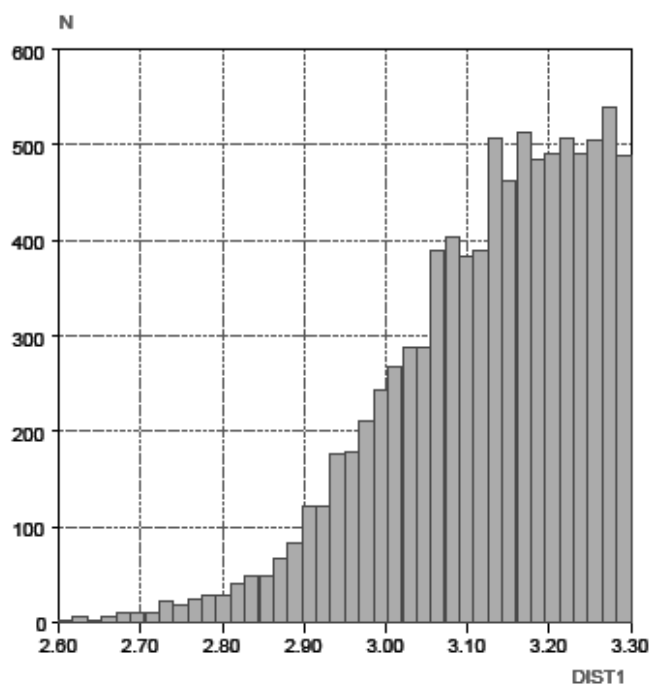
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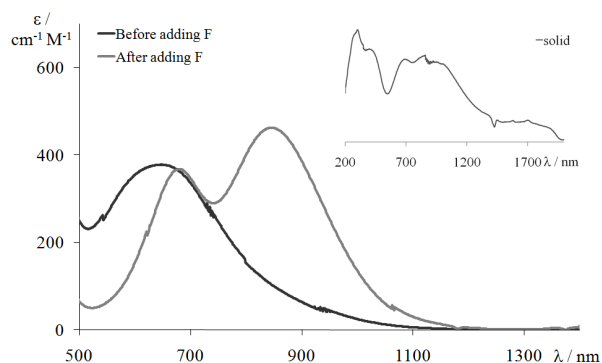
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**Fig. S1** Nitro-nitro interactions  $N2\cdots N4$  and  $N3\cdots N3$  shown as red dotted lines holding two individual complexes linked closely together.



**Fig. S2** Close  $O\cdots O$  distances in nitro-nitro interactions, based on 8889 observations in the CSD (version 5.29, Aug 2008).



**Fig S3** UV-vis-NIR spectra before (black line) and after (grey line) addition of 1 eq of tetraethylammonium fluoride (1.0 mM solutions). Inset shows the reflectance spectrum of the powdered solid.

**Table S1** Crystal data and details of the structure determination

<u>Crystal data</u>	
Formula	[CuC <sub>45</sub> H <sub>45</sub> N <sub>7</sub> O <sub>6</sub> F]BF <sub>4</sub> ·C <sub>4</sub> H <sub>8</sub> O,
Formula Weight	1021.34
Crystal System	Triclinic
Space group	$P\bar{1}$
$a / \text{\AA}$	9.2815(8)
$b / \text{\AA}$	14.958(1)
$c / \text{\AA}$	17.457(2)
$\alpha / ^\circ$	95.741(2)
$\beta / ^\circ$	92.388(2)
$\gamma / ^\circ$	104.621(2)
$V / \text{\AA}^3$	2327.8(4)
$Z$	2
$D_{\text{calc}} / \text{g cm}^{-3}$	1.457
$\mu / \text{mm}$	0.000
F(000)	1062
Crystal Size / mm	0.04 x 0.12 x 0.20
<u>Data collection</u>	
Temperature / K	150
Radiation / $\text{\AA}$	0.77490
$\theta_{\text{Min}}, \theta_{\text{Max}} / ^\circ$	2.6, 33.7
Index ranges min/max h,k,l	-13/13
	-21/21
	-24/24
Reflections collected	34376
Independent reflections	13933
$R_{\text{int}}$	0.060
Observed data with $I > 2.0\sigma(I)$	10521
<u>Refinement</u>	
Data/Parameters refined	13933/670
$R (I > 2.0\sigma(I))$	0.0566
$wR_2$ (all data)	0.1674
Largest diff. peak and hole / $\text{\AA}^{-3}$	-0.50, 0.66

## Experimental

### General

All solvents and reagents were obtained from commercial sources and used as received. The synthesis of the ligand (*p*-NO<sub>2</sub>BP)<sub>3</sub>tren has been reported elsewhere.<sup>1</sup> All manipulations were carried out in air. X-band EPR spectra were recorded on a Bruker EMX electron spin resonance spectrometer. EPR spectra were simulated using “The program EPR, a modelling approach”.<sup>2</sup> Solution UV-vis-NIR spectra were obtained on a Varian Cary 50 spectrophotometer (l = 1 cm) and diffuse reflectance spectrum of the solid was obtained on a Perkin-Elmer 330 spectrometer equipped with data station. FTIR spectra were obtained on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000 – 300 cm<sup>-1</sup>, res. 4 cm<sup>-1</sup>). C, H, N determinations were performed on a Perkin-Elmer 2400 Series II analyser.

*Crystal data collection and reduction.* The crystal was mounted in paratone oil. Data were collected on a Bruker AXS APEXII diffractometer on Station 11.3.1<sup>3</sup> of the Advanced Light Source, Lawrence Berkeley National Laboratory using silicon monochromated radiation of wavelength  $\lambda = 0.77490\text{\AA}$ , at 150 K; the instrument was fitted with an Oxford Cryostream low-temperature attachment. The Bruker AXS APEX 2 software was used throughout the data collection and reduction.

*Crystal structure solution and refinement.* The structure was solved by direct methods (SIR97<sup>4</sup> through WinGX<sup>5</sup>) and subjected to full-matrix least squares refinement on *F*<sup>2</sup>, using SHELXL. All non-hydrogen atoms were refined anisotropically. Geometrical and displacement parameter restraints were used to model the BF<sub>4</sub> group. Displacement parameter restraints were used in modelling one end of one of the ligand arms, even so the ratio of the displacement parameters max:min is around 5:1. Splitting the end of the arm was considered, but as it reflected the movement in the arm and no new chemical information would be gained, it was decided to leave it as it was. Hydrogen atoms were placed geometrically where possible and refined with a riding model. In the case of the N-H's, these were found in the difference map and these were allowed to refine with a restraint on the N-H distance.

### ***[Cu pNO<sub>2</sub>trenF]BF<sub>4</sub>·THF***

*Method 1:* A solution of (**p-NO<sub>2</sub>BP**)<sub>3</sub>tren (78 mg, 0.10 mmol) in 2 ml THF was added to a solution of Cu(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (35 mg, 0.10 mmol) in 1 ml of THF. Hexane was added to the resulting green solution and a precipitate formed which after a few hours produced an oil. The solution was concentrated and the crude oil was dissolved in THF and layered with ethanol. After four days, the mother solution was removed and [Cu(**p-NO<sub>2</sub>BP**)<sub>3</sub>trenF]BF<sub>4</sub>·xTHF (29 mg, 28%) was isolated as dark-green small single crystals suitable for X-ray crystallography.

*Method 2:* A solution of (**p-NO<sub>2</sub>BP**)<sub>3</sub>tren (78 mg, 0.10 mmol) in 2.5 ml of THF was added to a solution of Cu(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (35 mg, 0.10 mmol) in 2.5 ml of THF. Tetraethylammonium fluoride (19 mg, 0.10 mmol) in 1.5 ml of ethanol was added to the resulting dark-green solution while stirring. At the end of the addition, an obvious colour change to lighter green was observed. To the final solution, diethylether was added to precipitate a solid material. The mixture was left overnight, which resulted in a mixture of green and white crystals the next morning. The mother solution was removed and the solid was washed with water and diethyl ether and dried under vacuum to give [Cu(**p-NO<sub>2</sub>BP**)<sub>3</sub>trenF]BF<sub>4</sub>·THF as a green powder (68 mg, 67%). Elemental analysis: Found: C, 57.49; H, 5.41; N, 9.70. C<sub>49</sub>H<sub>53</sub>BCuF<sub>5</sub>N<sub>7</sub>O<sub>7</sub> requires: C, 57.62; H, 5.23; N, 9.60%; VIS-NIR reflectance λ<sub>max</sub>/nm = 690, 940; FT-IR: ν<sub>max</sub>/cm<sup>-1</sup> 3316(NH), 2875(br), 1600, 1515 (NO<sub>2</sub>), 1467, 1341, 1231, 1182, 1143, 1052(BF<sub>4</sub>), 942, 909, 870, 859, 745, 702 526.

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