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# Enhanced two-photon absorption cross-sections of zinc(II) tetraphenylporphyrins peripherally substituted with d<sup>6</sup>-metal alkynyl complexes†

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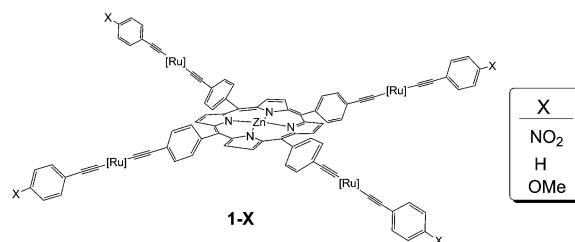
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The syntheses of new Zn(II) tetraphenylporphyrin (ZnTPP) derivatives functionalized with electron-rich d<sup>6</sup>-transition metal alkynyl complexes at their periphery are reported. Z-scan measurements reveal remarkably large effective two-photon absorption (TPA) cross-sections in the visible range for these compounds.

Molecules with significant TPA cross-sections have been attracting increasing attention over recent years because of the huge number of promising applications in emerging biophotonic and nanophotonic technologies that exploit this unusual third-order nonlinear optical (NLO) property.<sup>1,2</sup> The outstanding cubic NLO properties of porphyrins were recognized very early,<sup>3,4</sup> with several families of porphyrins being systematically screened for their TPA capabilities in the visible/near-IR range.<sup>5,6</sup> Among the various Zn(II) derivatives examined so far, some conjugated dimers were shown to possess remarkable TPA capabilities, while the corresponding monomeric Zn(II) porphyrin derivatives are usually much poorer two-photon absorbers.<sup>7–10</sup>

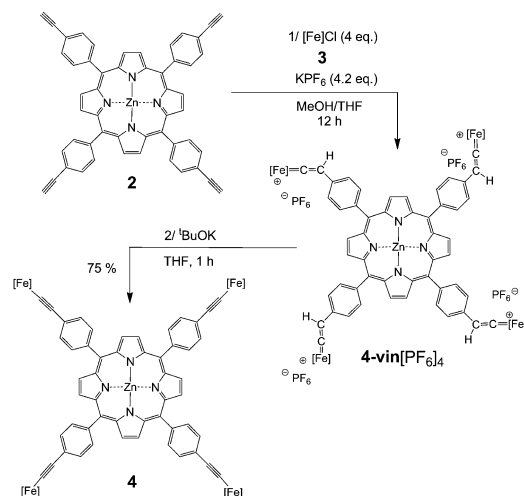
We have recently found that monomeric ZnTPP derivatives such as **1-X** (Scheme 1) exhibit quite large effective TPA cross-sections in the visible range, when peripherally functionalized



Scheme 1 Functional porphyrins **1-X** ([Ru] = *trans*-Ru(dppe)<sub>2</sub>).

with Ru(II) alkynyl complexes.<sup>11</sup> We now report the synthesis, characterization and Z-scan studies of two additional related derivatives, and confirm that peripheral organometallic substituents can strongly influence the effective two-photon absorption properties of these novel chromophores at selected wavelengths.

The synthesis of **4** was effected in two steps, *via* a vinylidene intermediate (**4-vin**)[PF<sub>6</sub>]<sub>4</sub>,<sup>12</sup> by reacting the known tetra-alkynyl porphyrin **2**<sup>11,13</sup> with the Fe(II) precursor **3**<sup>14</sup> (Scheme 2). The tetracationic vinylidene intermediate ( $\delta_P = 88.5$  ppm in the <sup>31</sup>P NMR and  $\nu_{Fe=C=C} = 1617$  cm<sup>-1</sup> in the IR) was not



Scheme 2 Synthesis of **4** ([Fe] = Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(dppe)).

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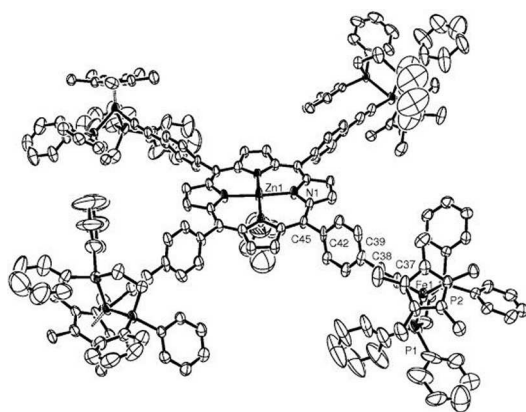
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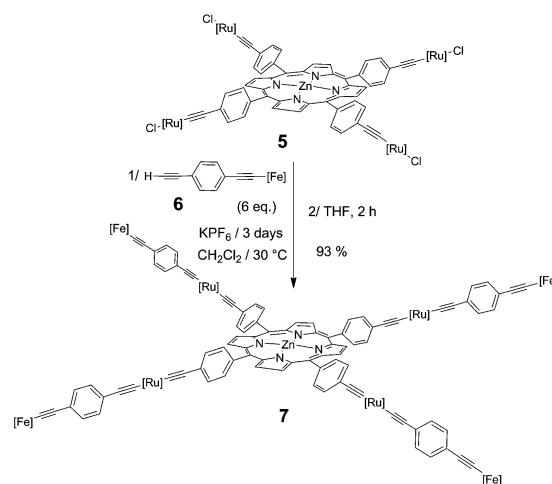
**Fig. 1** ORTEP of **4** (50 % probability level). Hydrogen atoms have been omitted for clarity. A disordered Et<sub>2</sub>O molecule coordinated to Zn is shown below the porphyrin plane.

purified, but rather was deprotonated directly after isolation to give the desired porphyrin **4** in 75% overall yield. The structure of **4** was confirmed by X-ray diffraction (Fig. 1).<sup>15</sup> Possibly due to slow desolvation of the pentane solvates or of the Et<sub>2</sub>O molecule coordinated to the Zn(II) atom of the porphyrin, no accurate elemental analysis of this compound was obtained, but the molecular ion peak was detected by ESI-HRMS as the di-, tri- and tetra-protonated species (ESI<sup>+</sup>).

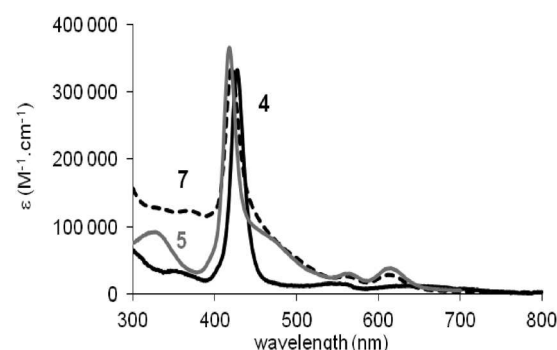
In the cyclic voltammogram, the oxidation of all Fe(II) endgroups was observed as a single and chemically reversible event at  $-0.15$  V vs. SCE (ESI<sup>+</sup>).<sup>16</sup> The corresponding Fe(III) tetracation **4**[PF<sub>6</sub>]<sub>4</sub> was isolated as a green solid after oxidation of **4** with four equivalents of [FcH][PF<sub>6</sub>]. A characteristic shift to lower wavenumbers of the  $\nu_{C\equiv C}$  is observed for **4**[PF<sub>6</sub>]<sub>4</sub> (1989 cm<sup>-1</sup>) compared to the corresponding band for **4**.<sup>17</sup> The <sup>1</sup>H NMR spectrum of **4**[PF<sub>6</sub>]<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub> reveals the expected Fe(III) alkynyl polyradical, with the *ortho* and *meta* protons of the *meso* phenyl groups resonating at  $-40.8$  and  $30.1$  ppm, respectively, and the pyrrolic protons as a singlet near  $10.5$  ppm (see ESI<sup>+</sup>).<sup>18</sup> The weak interaction between the unpaired electrons in this Fe-centered tetra-radical is indicated by ESR at 70 K; a rhombic spectrum was detected for **4**[PF<sub>6</sub>]<sub>4</sub> ( $g_1 = 2.024$ ,  $g_2 = 2.105$  and  $g_3 = 2.253$ ),<sup>19</sup> while a broad and featureless signal would have been observed in the case of strong spin–spin exchange coupling.<sup>20</sup>

Starting from **5**,<sup>11</sup> and from the known complex **6**,<sup>21</sup> the nonametallated porphyrin **7** featuring two alkynyl complexes in each branch was also synthesized (Scheme 3).<sup>22</sup> This compound (**7**) was isolated in good yield (93%) but, as seen with related compounds,<sup>13</sup> it could not be characterized by ESI- or MALDI-MS spectroscopy. However, a consistent set of spectral signatures was obtained from IR, <sup>31</sup>P and <sup>1</sup>H NMR, as well as diagnostic cyclic voltammograms, in which the Fe(II)- and Ru(II)-centered oxidations occur at  $-0.22$  V and  $0.44$  V vs. SCE in a chemically reversible way and with equal intensities (ESI<sup>+</sup>).

The UV-Vis absorption spectra of **4** and **7** were recorded in dichloromethane (Fig. 2). The strong Soret band near 420 nm is the source of the green color of these compounds. This band is slightly red-shifted in **4** compared to **7** and also to **5**, the latter compounds possessing spectra closer to those of **1-X** derivatives.<sup>11</sup>



**Scheme 3** Synthesis of **7** ([Fe] = Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(dppe) and [Ru] = *trans*-Ru(dppe)<sub>2</sub>).



**Fig. 2** UV-vis spectra of **4**, **5** and **7** (dotted line) in CH<sub>2</sub>Cl<sub>2</sub>.

The lowest-energy absorptions (near 550 and 620 nm) correspond to the porphyrin Q-bands; these are less intense, and blue- and red-shifted, respectively, for **4** relative to **7** and to **5**. The  $d_M \rightarrow \pi_{C\equiv C}^*$  MLCT bands (M = Fe, Ru) expected in the 400–300 nm range are obscured by the other absorptions.<sup>16</sup> The nonlinear absorption behavior of **4** and **7** were next measured in the spectral range of 600 to 1600 nm using Z-scan (ESI<sup>+</sup>), and were compared to those of the **1-X** derivatives (Table 1). The effective TPA cross-sections were then deduced from the imaginary part of the cubic hyperpolarizability  $\gamma$ . The latter exhibit a complicated wavelength-dependence, with three maxima and one minimum (Table 1), reminiscent of that previously observed for **1-X** derivatives.<sup>11</sup>

Due to the centrosymmetric nature of these porphyrins, the one-photon-allowed states cannot be involved in any TPA process because of the differing selection rules.<sup>11</sup> Nevertheless, the first maximum near 1100 nm for **4** and **1-X** compounds corresponds to excited TPA states in the porphyrin core Q-bands region while the minimum near 600 nm, which occurs at the wavelength of the one-photon band at lowest energy, certainly corresponds to a saturable absorption (SA) process involving this absorption band. The second TPA maximum occurs near 710 nm, with effective cross-sections up to 10 200 GM (for **4**); in contrast to the TPA process centered at 1100 nm, the  $\sigma_{2\text{eff}}$  values of the 710 nm TPA bands appear strongly influenced by the nature of the organometallic endgroups. Because the

**Table 1** Extremal values of the effective two-photon absorption cross-sections ( $\sigma_{\text{eff}}$ ) for given wavelengths<sup>a</sup>

Cpnd	1st max		2nd max		3rd max		1st min	
	$\lambda_{\text{max}}^b$	$\sigma_{\text{eff}}^c/\text{GM}$	$\lambda_{\text{max}}^b$	$\sigma_{\text{eff}}^c/\text{GM}$	$\lambda_{\text{max}}^b$	$\sigma_{\text{eff}}^c/\text{GM}$	$\lambda_{\text{max}}^b$	$\sigma_{\text{eff}}^c/\text{GM}$
<b>1-NO<sub>2</sub></b>	530	6000 ± 500	770	6000 ± 3000	1000	1500 ± 500	620	−4500 ± 200
<b>1-H</b>	—	—	710	4800 ± 500	1300	1400 ± 500	595	−2800 ± 600
<b>1-OMe</b>	< 530	3400 ± 500	710	4200 ± 500	1000	1300 ± 100	620	−1400 ± 400
<b>4</b>	570	6600 ± 1000	740	10 200 ± 1000	1000	600 ± 200	650	−6100 ± 1000
<b>7</b>	550	8900 ± 1500	740	8000 ± 500	— <sup>d</sup>	— <sup>d</sup>	620	−1500 ± 1000

<sup>a</sup> Measurements performed in dichloromethane. <sup>b</sup> In nm. <sup>c</sup> In Göppert-Mayer units (1 GM =  $1 \times 10^{-50} \text{ cm}^4 \text{ s}^{-1}$ ). <sup>d</sup> Not determined due to sample photodegradation.

largest cross-sections are found for **4** and **7**, which possess the more electron-rich metal center (M = Fe) connected to the porphyrin core, it is tempting to ascribe the excited state at the origin of the TPA process to a centrosymmetric  $d_M \rightarrow \pi_{C \equiv C}^*$  MLCT state (M = Fe, Ru),<sup>4,23</sup> located at *ca.* 350 nm.<sup>16</sup> Finally, the TPA maxima occurring at wavelengths below 600 nm, *i.e.* in an energy range where many excited states coexist, again exhibit the highest intensities for **4** and **7**. The excited states at the origin of these two-photon absorptions are more difficult to assign and necessitate calculations.

In conclusion, we report here the synthesis of two new ZnTPP derivatives functionalized at their periphery by “Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-(dppe)C $\equiv$ C” fragments. Moreover, we show that these new  $\pi$ -conjugated polynuclear assemblies incorporating electron-rich metal alkynyl fragments (**4** and **7**) exhibit TPA maxima at *ca.* 550 and 740 nm, with significantly larger effective cross-sections than analogous compounds featuring less electron-rich endgroups, such as bis-alkynyl “*trans*-Ru(dppe)<sub>2</sub>(C $\equiv$ CAr)C $\equiv$ C” fragments (**1-X**). Indeed, when compared to most of the monomeric Zn(II) porphyrin derivatives investigated to date,<sup>7,8</sup> much larger TPA cross-sections are found at technologically-significant wavelengths for these new organometallic derivatives, with effective cross-sections up to 10 200 GM for **4** at 740 nm. From the perspective of the practical use of TPA absorbers, the existence of a strong SA peak near 620 nm for **4** (−6100 GM) further widens the interest of this particular compound. Finally, preliminary investigations indicate that the tetracationic Fe(III) tetradical **4**[PF<sub>6</sub>]<sub>4</sub> possesses significant kinetic stability; work is now aimed at assessing the potential of **4** and **7** for electro-switching their remarkable cubic NLO properties.<sup>22,24</sup>

## Experimental

The reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were freshly distilled under argon using standard procedures.

### Compound 4

In an oven-dried Schlenk tube, ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(dppe)FeCl (**3**;<sup>14</sup> 0.225 g, 0.360 mmol), KPF<sub>6</sub> (0.075 g, 0.41 mmol), and the Zn(II) porphyrin **2**<sup>13</sup> (70 mg, 0.09 mmol) were suspended in a mixture of methanol and tetrahydrofuran (30 mL, v/v, 2:1) and stirred for 12 h at room temperature. After removal of the solvents, the residue was dissolved in 30 mL of dichloromethane in the presence of an excess of <sup>t</sup>BuOK (0.046 g, 0.41 mmol) and stirred for 2 h at room temperature. After removal of the solvent, the dark residue was extracted with

toluene and the extract concentrated *in vacuo*. Several washings with diethyl ether removed the excess of **2** and yielded the air-sensitive complex **4** as a green solid (211 mg, 75%). X-Ray-quality crystals were grown by slow diffusion of pentane into a CH<sub>2</sub>Cl<sub>2</sub> solution of **4**. HRMS (ESI, MeOH-CH<sub>2</sub>Cl<sub>2</sub>, *m/z*): [M + 2H]<sup>2+</sup> calc. for C<sub>196</sub>H<sub>182</sub>Fe<sub>4</sub>N<sub>4</sub>P<sub>8</sub>Zn 1563.4477, found: 1563.4472 (10%); [M + 4H]<sup>4+</sup> calc. for C<sub>196</sub>H<sub>184</sub>Fe<sub>4</sub>N<sub>4</sub>P<sub>8</sub>Zn 782.2278, found: 782.2274 (100%). IR ( $\nu$ , KBr-CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>−1</sup>): 2043/2052 (*vs.* FeC $\equiv$ C). <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$  in ppm): 101.7 (broad s, 8P, (dppe)Fe). <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$  in ppm): 9.21 (s, 8H, *H* <sub>$\beta$ -pyrrolic), 8.22 (s, 24H, *H*<sub>Ph/dppe</sub> + *H*<sub>Ar</sub>), 7.64 (d, 8H, <sup>3</sup>*J*<sub>H,H</sub> = 7.6 Hz, *H*<sub>Ar</sub>), 7.50–7.00 (m, 64H, *H*<sub>Ar/dppe</sub> + *H*<sub>phenyl</sub>), 2.90 (m, 8H, *CH*<sub>2</sub>), 1.88 (m, 8H, *CH*<sub>2</sub>), 1.66 (s, 60H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$  in ppm):<sup>15</sup> 151.3 (s, C $\alpha$ -pyrrolic), 139.9 (t, <sup>3</sup>*J*<sub>P,H</sub> = 38 Hz, Fe-C $\equiv$ C), 139.6 (s, C<sub>Ar</sub>[C<sub>6</sub>]), 140.6 and 138.8 (2  $\times$  s, C<sub>i/dppe</sub>), 136.1 (s, CH<sub>Ar</sub>[C<sub>6</sub>]), 135.4 and 135.1 (2  $\times$  broad s, 2CH<sub>O/dppe</sub>), 132.8 (s, CH $\beta$ -pyrrolic), 131.2 (s, C<sub>Ar</sub>[C<sub>d</sub>]), 130.1 and 129.5 (2  $\times$  broad s, CH<sub>p/dppe</sub>), 129.3 (s, CH<sub>Ar</sub>[C<sub>d</sub>]), 128.3 and 128.1 (2  $\times$  broad s, 2CH<sub>m/dppe</sub>), 122.5 (s, C<sub>meso</sub>), 121.5 (broad s, Fe-C $\equiv$ C), 88.6 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 31.9 (m, CH<sub>2/dppe</sub>), 11.3 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , ( $\epsilon$ , 10<sup>3</sup> M<sup>−1</sup> cm<sup>−1</sup>), nm): 351 (34), 428 (330), 537 (16), 635 (15). CV (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>], 20 °C, 0.1 V s<sup>−1</sup>, *E*<sup>o</sup> in V *vs.* SCE): −0.14, 0.88.</sub>

### Compound 7

In a Schlenk tube, the tetraruthenium porphyrin complex **5**<sup>11</sup> (100 mg, 0.022 mmol), the iron compound (dppe)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-FeC $\equiv$ C(1,4-C<sub>6</sub>H<sub>4</sub>)C $\equiv$ CH (**6**;<sup>21</sup> 95 mg, 0.13 mmol) and KPF<sub>6</sub> (24.5 mg, 0.142 mmol) were dissolved in 30 mL of dichloromethane and stirred for 3 days at 30 °C. After removal of the solvent, the green residue was dissolved in THF in the presence of an excess of <sup>t</sup>BuOK (11 mg, 0.01 mmol) and stirred for 3 h at room temperature. After evacuation of the solvent, the product was extracted with toluene; the solution was concentrated and washed with Et<sub>2</sub>O to afford the complex **7** (150 mg, 0.020 mmol, 93%) as an air-sensitive green solid. IR ( $\nu$ , KBr, cm<sup>−1</sup>): 2047 (*vs.* FeC $\equiv$ C + RuC $\equiv$ C). <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$  in ppm): 101.8 (s, 8P, (dppe)Fe), 55.1 (s, 16P, (dppe)<sub>2</sub>Ru). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$  in ppm): 9.41 (s, 8H, *H* <sub>$\beta$ -pyrrolic), 8.40 (d, 8H, <sup>3</sup>*J*<sub>H,H</sub> = 6.3 Hz, *H*<sub>Ar</sub>), 8.12 (m, 16H, *H*<sub>Ar/dppe</sub>), 7.87 (m, 48H, *H*<sub>Ar/dppe</sub>), 7.57 (d, 8H, <sup>3</sup>*J*<sub>H,H</sub> = 6.6 Hz, *H*<sub>Ar</sub>), 7.45–6.80 (m, 192H, *H*<sub>Ar/dppe</sub> + *H*<sub>Ar</sub>), 2.72 (m, 32H, CH<sub>2/dppe</sub>/Ru), 2.59 (m, 8H, CH<sub>2/dppe</sub>/Fe), 1.89 (m, 8H, CH<sub>2/dppe</sub>/Fe), 1.59 (s, 60H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$  nm ( $\epsilon$ , 10<sup>3</sup> M<sup>−1</sup> cm<sup>−1</sup>)): 351 (98), 424 (347), 560 (24), 614 (28). CV (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>], 20 °C, 0.1 V s<sup>−1</sup>, *E*<sup>o</sup> in V *vs.* SCE): −0.22, 0.44.</sub>



## Compound 4[PF<sub>6</sub>]<sub>4</sub>

In a Schlenk tube, **4** (150 mg, 0.048 mmol, 1.0 eq.) and [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] (64 mg, 0.193 mmol, 4.0 eq.) were stirred for 1 h at 25 °C in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). After partial removal of the solvent (*ca.* 5 mL), pentane was added (60 mL), the mixture was filtered, and the solvent was removed. The residue was then washed with thoroughly degassed toluene (2 mL) and pentane (2 mL) at 0 °C to obtain the title tetracation 4[PF<sub>6</sub>]<sub>4</sub> complex as a dark green solid (89 mg, 50%). IR (KBr–CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>−1</sup>):  $\nu$  = 1986/1989 (w, FeC $\equiv$ C), 839/846 (vs. PF<sub>6</sub><sup>−</sup>). <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 30.1 (m, 1H, CH<sub>Ar</sub>[C<sub>2</sub>]), 10.5 (s, 1H, CH <sub>$\beta$ -Pyrrole</sub>), 8.0 (s, 2H, H<sub>Ph-dppe</sub>), 7.0 (m, 8H, H<sub>Ph-dppe</sub>), 6.4 (m, 2H, H<sub>Ph-dppe</sub>), 3.7 (s, 4H, H<sub>Ph-dppe</sub>), 1.9 (s, 4H, H<sub>Ph-dppe</sub>), −2.7 (m, 2H, CH<sub>2-dppe</sub>), −10.2 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), −40.8 (broad s, 1H, CH<sub>Ar</sub>[C<sub>1</sub>]).

## X-Ray crystallography

Diffraction data frames for **4** were collected on a CCD Sapphire 3 Xcalibur diffractometer at 120(2) K using Mo–K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved with a crystallographically imposed  $\bar{4}$  symmetry by direct methods using the SIR97 program,<sup>25</sup> and then refined with full-matrix least-square methods based on  $F^2$  (SHELX-97)<sup>26</sup> with the aid of the WINGX<sup>27</sup> program. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were then included in calculated positions. A final refinement on  $F^2$  with 9916 intensities ( $I > 2\sigma(I)$ ) and 522 parameters converged at  $wR(F^2)$  = 0.3241 ( $R(F)$  = 0.1684). Crystal data: C<sub>200</sub>H<sub>190</sub>Fe<sub>4</sub>N<sub>4</sub>O<sub>8</sub>P<sub>8</sub>Zn<sub>4</sub>C<sub>5</sub>H<sub>12</sub>,  $M$  = 3490.67, tetragonal, space group  $I$  4<sub>1</sub>/a,  $a$  = 36.9262(5) Å,  $b$  = 36.9262(5) Å,  $c$  = 14.7933(8) Å,  $U$  = 20171.3(12) Å<sup>3</sup>,  $Z$  = 4,  $T$  = 120(2) K,  $D_c$  = 1.140 g cm<sup>−3</sup>, 124 170 reflections measured, 9916 unique ( $R_{int}$  = 0.0699) which were used in calculations.  $R$  was 0.1169 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  was 0.3301 (all data). CCDC 884562.

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