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# Two-photon spectroscopy of tungsten(0) arylisocyanides using nanosecond-pulsed excitation<sup>†</sup>

Kana Takematsu,<sup>a,b</sup> Sara A. M. Wehlin,<sup>a,c</sup> Wesley Sattler,<sup>a,d</sup> Jay R. Winkler <sup>(b)</sup> \*<sup>a</sup> and Harry B. Gray\*<sup>a</sup>

Received 19th July 2017, Accepted 11th September 2017 DOI: 10.1039/c7dt02632c The two-photon absorption (TPA) cross sections ( $\delta$ ) for tungsten(0) arylisocyanides (W(CNAr)<sub>6</sub>) were determined in the 800–1000 nm region using two-photon luminescence (TPL) spectroscopy. The complexes have high TPA cross sections, in the range 1000–2000 GM at 811.8 nm. In comparison, the cross section at 811.8 nm for tris-(2,2'-bipyridine)ruthenium(II), [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, is 7 GM. All measurements were performed using a nanosecond-pulsed laser system.

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## Introduction

The many potential applications of two-photon absorption (TPA) (e.g., microscopy, photodynamic therapy, microfabrication, and optical power limiting) have stimulated efforts to discover new compounds with large TPA cross sections  $(\delta)$ .<sup>1-6</sup> Notably, owing in part to the enhancement of TPA cross sections in molecules with  $\pi$ -conjugated chains, organic macromolecular and dendrimer chromophores have received much attention.<sup>2,7-9</sup> In addition, over the past twenty years, there have been many studies exploring coordination complexes that combine the chemical stability and tunability of metal centers with a diverse library of ligands and linking polymers that could potentially promote TPA.<sup>10-23</sup> Early TPA studies of inorganic chromophores found disappointing cross sections compared to those of well-designed organic chromophores ( $\delta >$ 1000 GM): the TPA cross section of the popular tris-(2,2'-bipyridine)Ru(II) ion ([Ru(bpy)<sub>3</sub>]<sup>2+</sup>) was reported to be just 4.3 GM at 880 nm.<sup>10</sup> Imaginative designs of transition metal complexes have led to striking improvements in TPA cross sections: oligo (p-phenylenevinylene) groups end-functionalized by Rualkynyl groups have  $\delta > 12500$  GM (at 725 nm), although the chromophore is localized on the phenylenevinylene moiety.<sup>18</sup>

<sup>a</sup>Beckman Institute, California Institute of Technology, Pasadena CA 91125, USA. E-mail: winklerj@caltech.edu, hbgray@caltech.edu

<sup>b</sup>Department of Chemistry, Bowdoin College, Brunswick, ME 04011, USA

The strong one-photon absorption cross sections and relatively long lifetimes ( $\sim \mu s$ ) of metal-ligand charge transfer (MLCT) states suggest that metal-acceptor(ligand) complexes represent attractive targets for TPA applications that could potentially combine the desired redox chemistry from one-photon chemistry with the enhanced spatial resolution and increased penetration depth from two-photon chemistry.

With the exception of metalloporphyrins,<sup>1,19</sup> most TPA studies of inorganic complexes or templates have employed ruthenium as the central metal.<sup>10-18</sup> A handful of other metal chromophores have been explored, including ones containing lanthanide ions, Re, Ir, Fe, Pt, and Zn.<sup>11,13,20-28</sup> Further development of transition metal TPA complexes will be required if they are to compete with organic chromophores. With this objective in mind, we chose to work on homoleptic tungsten arylisocyanide complexes (W(CNAr)<sub>6</sub>) that exhibit intense onephoton absorption bands in the visible region and relatively long excited-state lifetimes.<sup>29-32</sup> The tungsten complex,  $W(CNdipp)_6$  (CNdipp = 2,6-diisopropylphenyl-isocyanide), is a strong photoreductant  $(E^{\circ}(W^{+}/*W^{0}) = -2.8 \text{ V } \nu s. \text{ Cp}_{2}\text{Fe}^{+/0}$  in THF), making it of interest as a photoredox sensitizer.<sup>29</sup> Derivatization of CNdipp, shown in Fig. 1, resulted in tungsten complexes with longer lifetimes ( $\tau = 75 \text{ ns} - 1.56 \text{ }\mu\text{s}$  in THF) and relatively high luminescence quantum yields ( $\Phi$  = 0.01-0.25 in THF).32 The extended conjugation of the nearly coplanar  $\pi$ -systems in crystal structures suggests that these molecules are promising TPA candidates.

Two main methods have been used to obtain TPA cross sections. In *z*-scan,<sup>33</sup> the transmitted light intensity is measured as the sample is moved between focal points of the laser source and detector. In two-photon luminescence (TPL), once called two-photon-excitation fluorescence (TPEF),<sup>34</sup> emission spectra are collected as the sample is excited by a tightly



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<sup>&</sup>lt;sup>c</sup>Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

<sup>&</sup>lt;sup>d</sup>The Dow Chemical Company, Formulation Science, Core R&D, 400 Arcola Road, Collegeville, PA 19426, USA

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**Fig. 1** Top: Tungsten(0) (oligo)arylisocyanide W(CNAr)<sub>6</sub>. Bottom: (Oligo) arylisocyanides CNdipp, CNdippPh, CNdippPh<sup>Ph</sup>, and CNdippPh<sup>OMe<sub>2</sub></sup>.

focused beam from a pulsed laser. In relative TPL measurements, the TPL cross sections are determined by comparison to standard or reference TPL dyes.<sup>34–36</sup> The TPA cross sections are extrapolated from TPL measurements, assuming similar one-photon and two-photon photoluminescence quantum efficiencies ( $\Phi$ ):  $\delta = \Phi^{-1}\sigma_{\text{TPL}}$ .

Both methods typically utilize ultrafast Ti:sapphire lasers for temporal and spatial control of the light source. Despite the lowering cost and ready commercial availability of femtosecond lasers, they remain a hurdle for many researchers interested in pursuing TPA studies. Even with access, the additional cost and difficulty of realigning wavelength-dependent optics tend to limit TPA studies to single wavelength measurements. Comparing the two methods, TPL is less demanding in terms of laser pulse-width;37 indeed, the first evidence of TPL was obtained in 1961 via detection of Eu2+ luminescence produced by excitation with a nanosecond pulsed ruby laser.<sup>38</sup> In 2000, Rumi et al. showed that TPA cross sections obtained via TPL using nanosecond and picosecond lasers were approximately the same for organic chromophores (bis-dialkylamino- and diarylamino-substituted diphenylpolyenes and bis(styryl) benzenes).<sup>37</sup> Although nanosecond lasers were used in early TPA studies, they have largely been replaced by femtosecond excitation sources. Nevertheless, TPL measurements with nanosecond pulsed lasers can provide reliable cross sections and absorption spectra.

We report here our application of a pulsed Nd:YAG laser optical parametric oscillator combination to obtain an extended TPA spectrum for  $[Ru(bpy)_3]^{2+}$ , and TPA cross sections for tungsten(0) arylisocyanides W(CNdipp)<sub>6</sub>, W(CNdippPh)<sub>6</sub>, W(CNdippPh<sup>Ph</sup>)<sub>6</sub>, and W(CNdippPh<sup>OMe</sup><sub>2</sub>)<sub>6</sub>.

## Experimental

#### Sample preparation

The arylisocyanide ligands (CNAr, Ar = aryl groups including dipp and *para*-modified dipp groups dippPh, dippPh<sup>Ph</sup>, and

dippPh<sup>OMe<sub>2</sub></sup> as shown in Fig. 1) and corresponding tungsten complexes, W(CNAr)<sub>6</sub>, were synthesized and purified according to previously published protocols.<sup>29,32</sup> Briefly, all ligands were synthesized from a single intermediate, N-formyl-4-bromo-2,6diisopropylaniline, by Suzuki coupling of an arylboronic acid followed by dehydration with OPCl<sub>3</sub>. WCl<sub>4</sub>(THF)<sub>2</sub> was then reduced with Na(Hg) in the presence of the ligands to produce the respective tungsten complexes. Solutions of the tungsten complexes were prepared in a nitrogen-filled glovebox using 2-methyltetrahydrofuran (2MTHF) that was freshly distilled from Na/benzophenone ketyl for experiments. Immediate UVvis spectra (Cary 50) were collected in 1 mm cuvettes upon removal from the glovebox. Solutions for TPA experiments were placed in custom-made long-neck 1 cm cuvettes and flame-sealed on a high-vacuum line upon removal from the glovebox. Sample concentrations of W(CNdipp)<sub>6</sub>, W(CNdippPh)<sub>6</sub>, W(CNdippPh<sup>Ph</sup>)<sub>6</sub>, and W(CNdippPh<sup>OMe<sub>2</sub></sup>)<sub>6</sub> ranged from 5–25 µM. All samples were stored in the dark.

 $[Ru(bpy)_3]Cl_2$  and our emission standard, fluorescein, were obtained from Sigma Aldrich and used without further purification. Sample solutions  $([Ru(bpy)_3^{2^+}] = 5 \text{ mM}; [fluorescein] = 78 \mu\text{M})$  for TPL measurements were prepared in MilliQ water and filtered with Millex GV filters (0.22  $\mu$ m). The fluorescein solution was adjusted to pH 11 using NaOH (1 M). The solutions were placed in modified Schlenk cuvettes (1 cm) and were degassed and backfilled with argon. All samples were stored in the dark before measurement.

#### Laser apparatus

Spectral experiments were performed in the Beckman Institute Laser Resource Center (BILRC). The third harmonic (355 nm) from a Q-switched Nd:YAG laser (Spectra-Physics Quanta Ray PRO, 10 Hz, 8 ns pulse) pumped a tunable optical parametric oscillator (OPO, Spectra-Physics Quanta Ray MOPO-700). A Pellin-Broca prism mounted on a rotational stage separated the visible and near infrared (NIR) components. Two broadband mirrors (Newport) directed the preferred component to the sample holder (1 cm cuvette holder with a magnetic stirrer). The visible OPO output was used for initial beam alignment; two 1.5 cm apertures were introduced to the beam path to fix the radius and aid in the alignment of the NIR beam. A NIR detector card (Thorlabs VRC4) was then used to adjust the Pellin-Broca prism such that the NIR output (820 nm) was centered on the first broadband mirror. A 700 nm long pass filter was introduced to eliminate residual interference from the visible laser light, and spherical lens (100 or 25 cm focal length) was added to concentrate the beam.

Excitation wavelength tuning only required OPO adjustment and rotation of the Pellin-Broca prism stage. A power-meter was placed before the sample to optimize the NIR alignment using the rotation stage. A small fraction of the excitation beam was picked off and recorded with a calibrated Si photodiode detector to provide precise readouts at low excitation powers. Steady-state emission spectra were collected at a 90° angle from the excitation path *via* a 2-in collection lens and an optical fiber attached to a spectrometer (Melles-Grigot 13 FOS200). The integration times for each relative emission spectrum varied by sample:  $[Ru(bpy)_3]Cl_2$  (8000 ms),  $W(CNdipp)_6$ (20 000–30 000 ms),  $W(CNdippPh)_6$  (1000–1500 ms),  $W(CNdippPh^{Ph})_6$  (5000–12 000 ms), and  $W(CNdippPh^{OMe_2})_6$ (600–1500 ms). At each excitation wavelength, four spectra were collected, averaged, and corrected for the dark noise and spectrometer response.

A typical TPL experiment consisted of spectral collection over 800–1050 nm of the sample of interest. The excitation wavelengths were scanned in random order to minimize systematic bias in the laser power. All emission data were collected and analyzed in Matlab (The MathWorks, Inc.) to determine the TPA cross section ( $\delta$ ) according to eqn (1),<sup>34</sup> where  $\alpha$  is a scaling factor independent of the chemical identity of the sample and

$$\delta = \alpha \frac{\langle F(t) \rangle}{\lambda \Phi C n \langle P(t) \rangle^2} \tag{1}$$

includes the effects of the beam profile, sample excitation, and collection efficiency,  $\lambda$  is the wavelength of the excitation light,  $\Phi$  = photoluminescence quantum efficiency, C = concentration, n = index of refraction of the solvent, (P(t)) = time-averaged power of the laser, and (F(t)) = time-averaged emission intensity. To generate absolute TPA spectra, reference (fluorescein) and sample luminescence spectra were collected with 811 nm excitation using a fixed geometry (ESI<sup>†</sup>). There is some variability in reported values of  $\delta_{811}$  for fluorescein;<sup>35,36,39</sup> we chose the smallest value ( $\delta_{811}$  = 21 GM (ref. 39)) to determine the scaling factor  $\alpha$ . Owing to the sensitivity of these measurements to several experimental parameters, we estimate that the uncertainties in the TPA cross sections are as large as 30%. The TPA spectrum of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in deionized water was determined from relative TPL measurements, and scaled to the previously reported cross section ( $\delta_{880 \text{ nm}} = 4.3$ ).<sup>10</sup> The quantum yields for the tungsten complexes in THF are: W(CNdipp)<sub>6</sub> ( $\Phi = 0.01$ ), W(CNdippPh)<sub>6</sub> ( $\Phi = 0.21$ ), W(CNdippPh<sup>Ph</sup>)<sub>6</sub> ( $\Phi = 0.07$ ), and W(CNdippPh<sup>OMe<sub>2</sub></sup>)<sub>6</sub> ( $\Phi =$ 0.21).<sup>32</sup> Quantum yields for the tungsten complexes in 2MTHF were determined from the ratio of the lifetimes  $(\tau)$  of the excited state in THF and 2MTHF assuming that the radiative rate constants  $(k_r)$  are the same in the two solvents (eqn (2)). Smoothed two-photon absorption cross sections were generated using a Savitzky-Golar algorithm implemented in Matlab using a polynomial order of 3 and a frame length of 11. A table of experimental details is given in ESI.†

$$\frac{\Phi_{\mathrm{W}(\mathrm{CNAr})_{6}:2\mathrm{MTHF}}}{\Phi_{\mathrm{W}(\mathrm{CNAr})_{6}:\mathrm{THF}}} = \frac{k_{\mathrm{r}}\tau_{\mathrm{W}(\mathrm{CNAr})_{6}:2\mathrm{MTHF}}}{k_{\mathrm{r}}\tau_{\mathrm{W}(\mathrm{CNAr})_{6}:\mathrm{THF}}} = \frac{\tau_{\mathrm{W}(\mathrm{CNAr})_{6}:2\mathrm{MTHF}}}{\tau_{\mathrm{W}(\mathrm{CNAr})_{6}:\mathrm{THF}}}$$
(2)

Power-dependent luminescence measurements were made to verify TPA. Laser power was attenuated by either addition of neutral density filters or by minor tuning of the Nd:YAG harmonic-generating crystal. For time-resolved measurements, sample luminescence was directed by optical fiber to the entrance slit of a double monochromator (Instruments SA DH-10) and detected by a PMT (Hamamatsu R928). Data were recorded with and without laser excitation and processed in Labview. Details of the time-resolved luminescence instrumentation and electronics have been published.<sup>32</sup>

## Results and discussion

Validation of the laser apparatus was performed using fluorescein, a TPL standard. Scaled TPA spectra of fluorescein from multiple data sets were in reasonable agreement with reference spectra collected using femtosecond-pulsed lasers in the 800–900 nm region (Fig. 2).<sup>35,36,39</sup> The variations among the three published TPA spectra of fluorescein illustrate the challenges associated with these measurements. Slight discrepancies in our data at longer wavelengths could arise from instability of the laser output. To cover the broad spectral profile, previous studies required the interchange of multiple optical elements, which may have introduced some error in the spectral data. The reproducibility of the spectral contour, the broad spectral window, and ease of alignment of Nd:YAG/ OPO apparatus were all well-suited for our experiments.

Power-dependent studies of fluorescein,  $[Ru(bpy)_3]^{2+}$ , and  $W(CNAr)_6$  complexes at  $\lambda_{exc} = 847.6$  nm all showed quadratic dependence on the excitation power (ESI<sup>†</sup>). Emission spectra and time-resolved emission decays at 610 nm collected under one and two-photon excitation showed no major discrepancies (ESI<sup>†</sup>). These results are consistent with the earlier work on  $[Ru(bpy)_3]^{2+}$  by Castellano *et al.*<sup>10</sup> For the W(CNAr)<sub>6</sub> complexes, the decays in 2MTHF were slightly longer than those in THF:  $W(CNdippPh)_6: \tau = 1.55 \ \mu s \ vs. \ 1.32 \ \mu s, W(CNdippPh^{Ph})_6: \tau = 610 \ ns \ vs. \ 350 \ ns, W(CNdippPh^{OMe_2})_6: \tau = 1.47 \ \mu s \ vs. \ 1.20 \ \mu s.^{32}$  The lifetime ratios were used to adjust the quantum yields for TPA spectral analysis. The long  $W(CNAr)_6 \ MLCT$  lifetimes under two-photon excitation likely will be exploited in future applications.



**Fig. 2** TPA spectra of fluorescein. The reproducibility of the data and agreement with the reference data are shown in the figure. Each set of symbols corresponds to a different data collection date, while the solid, dashed, and dot-dashed lines correspond to the spectra in ref. 39, 35, and 36, respectively.

The TPA spectrum of  $[Ru(bpy)_3]Cl_2$  is shown in Fig. 3. The spectral region corresponds to the excitation of the MLCT band. Comparison with the single-photon absorption spectrum showed a blue-shift in the TPA spectrum. This shift has been observed in previous TPA experiments.<sup>34</sup>

What about TPA cross sections for other Ru(II) complexes? Values for complexes with *N*-methyl/aryl-2,2':4,4":4',4"-quaterpyridinium,<sup>13</sup> fluorene-substituted 1,10-phenanthroline,<sup>12</sup> and a combination of phenanthroline and dipyridophenzine ligands<sup>11</sup> are somewhat greater than those for [Ru(bpy)<sub>3</sub>]<sup>2+</sup>:  $\delta$  = 62–180 GM at 720 nm,  $\delta$  = 90/15/15 GM at 750/850/930 nm, and  $\delta$  = 150 GM at 710 nm, respectively. If the TPA cross sections are corrected for molecular weight ( $\delta$ /M or GM mol g<sup>-1</sup>),<sup>40</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> could potentially be a better TPA chromophore on a per mass basis at selected wavelengths.

Interestingly, the TPA cross sections of Ru(II) complexes can be tuned by the degree of  $\pi$ -conjugation in the ligands, but the enhancement appears largely to arise from intraligand charge transfer (ILCT) rather than MLCT interactions. After installing a triple bond between ligating phenanthroline and fluorene groups, Girardot *et al.* observed an ILCT band at 400 nm, leading to increased TPA cross sections in the 700–900 nm region.<sup>12</sup> In addition, examining dimeric versions of [Ru(phen)<sub>2</sub>dppz]<sup>2+</sup>, Samoc *et al.* observed significant enhancement in the ILCT excitation region (560 nm) but not at 710 nm (MLCT).<sup>14</sup> In-depth comparisons of experimental TPA results with electronic structure calculations for [Ru(bpy)<sub>3</sub>]<sup>2+</sup> would shed light on the ILCT and MLCT states and could lead to the design and construction of metal complexes with greatly enhanced TPA cross sections.

The TPA spectra of W(CNdippPh)<sub>6</sub>, W(CNdippPh<sup>Ph</sup>)<sub>6</sub>, and W(CNdippPh<sup>OMe<sub>2</sub></sup>)<sub>6</sub> are all blue-shifted from one-photon absorptions (Fig. 4). The TPA spectrum for W(CNdipp)<sub>6</sub> could not be collected, owing to the relatively low quantum yield ( $\Phi \sim 0.01$ ). The TPA cross sections for the remaining complexes are exceptionally high (Table 1), in the range of 1000–2000 GM at 811.8 nm. Comparisons to one-photon absorption spectra suggest that the cross sections could increase further at



**Fig. 3** TPA spectra of  $[Ru(bpy)_3]^{2+}$ . The open markers correspond to different experimental sets. The solid line is a smoothed curve produced using a Savitzky–Golay filter (order 3, frame 11) through the average of the data sets. The dashed line is the one-photon absorption spectrum for  $[Ru(bpy)_3]^{2+}$ .



**Fig. 4** From top to bottom: TPA spectra of W(CNdippPh)<sub>6</sub>, W(CNdippPh<sup>Ph</sup>)<sub>6</sub>, and W(CNdippPh<sup>OMe<sub>2</sub></sup>)<sub>6</sub>. For each panel, the markers correspond to different experimental sets. The solid lines are smoothed curves produced using a Savitzky–Golay filter (order 3, frame 11) through the averages of each data set. The dashed lines are the one-photon absorption spectra. For the middle panel, the data set ( $\bigcirc$ ) was collected with slightly unstable laser power at the edge of the scans; a second data set ( $\bigcirc$ ) was collected when the laser power was more stable. The data sets were scaled and the long wavelength baselines were matched; no other corrections were made to the data.

Table 1Comparison of one-photon and two-photon absorption crosssections for tungsten arylisocyanides in 2MTHF

Complex	$\lambda_{\rm OP}^{a}$ (nm)	$ \begin{array}{c} \varepsilon \times 10^{-4 a} \\ (\mathrm{M}^{-1} \mathrm{ cm}^{-1}) \end{array} $	$\lambda_{\mathrm{TP}}$ (nm)	δ (GM)
W(CNdippPh) <sub>6</sub>	406, 497	4.3, 13	811.8	2000
W(CNdippPh <sup>Ph</sup> ) <sub>6</sub>	406, 508	4.0, 16	811.8	1700
W(CNdippPh <sup>OMe</sup> 2) <sub>6</sub>	406, 498	4.5, 13	811.8	1000

<sup>*a*</sup> Wavelengths corresponding to the two-photon absorption and maximum MLCT bands; extinction coefficients are in ref. 29.

shorter wavelengths. These values, which are larger than those reported for many organic chromophores, are comparable to some of the highest TPA cross sections of metal complexes.<sup>17,18</sup> If MWs of the species were included (or as suggested by others, numbers of electrons),<sup>41,42</sup> the weighted TPA cross sections could be even higher.

The large TPA cross sections of tungsten(0) complexes can be understood in terms of elements that optimize TPA in dyes: (1) centrosymmetric geometry; (2) extended  $\pi$ -conjugation in the ligands; (3) strong one-photon absorption near the TPA band.<sup>1</sup> Previously published W(CNAr)<sub>6</sub> solid-state structures showed that the compounds are all nearly centrosymmetric.<sup>32</sup> The *trans*-arylisocyanide ligands are oriented in a coplanar manner, constrained by bulky ortho-isopropyl groups. These ligands therefore form a fully conjugated  $\pi$ -system. TDDFT calculations indicate that the MLCT excited states in these molecules involve a transfer of charge from the metal centers onto the ligands.43 These MLCT excited states are threefold degenerate in  $O_{\rm h}$  or  $T_{\rm h}$  symmetry; this degeneracy contributes to the large extinction coefficients and two-photon cross sections. Comparison of the TPA spectra showed that neither the addition of phenyl or methoxy groups to CNdippPh significantly altered the cross sections. As the maximum one-photon absorption of W(CNdippPh<sup>Ph</sup>)<sub>6</sub> (Table 1) is red-shifted compared to the other complexes, it is possible that at other wavelengths the complex may have slightly higher TPA cross sections ( $\lambda$  < 811.8 nm). The addition of a phenyl group to CNdipp most likely increased the TPA cross sections, however, due to the poor quantum yield of W(CNdipp)<sub>6</sub>, the enhancement could not be directly measured using TPL.

The UV/vis spectra of the W(CNAr)<sub>6</sub> complexes exhibited strong MLCT absorptions, with extinction coefficients an order of magnitude larger (Table 1) than that for the MLCT band in  $[Ru(bpy)_3]^{2+}$  (1.45 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> at 452 nm).<sup>44</sup> Sattler *et al.* suggested that the intensity of the bands was due to significant CT character in both the ground and excited states, W 5d $\pi$  – CN  $\pi^*$  and W 6p – CN  $\pi^*$ , respectively.<sup>32</sup> Upon excitation, the molecule slightly distorts, increasing its net dipole moment. As relaxation of the excited state is solvent-dependent, the dependence of the TPA cross section on solvent polarity should be examined further to see whether there is competition between the distortion of the excited state to increase the net dipole change and conservation of the constrained molecular symmetry to preserve  $\pi$ -conjugation in the ligands.

## Concluding remarks

The TPA cross sections corresponding to MLCT excitation regions in W(CNdippPh)<sub>6</sub>, W(CNdippPh<sup>Ph</sup>)<sub>6</sub>, and W(CNdippPh<sup>OMe<sub>2</sub></sup>)<sub>6</sub> determined from 800–1000 nm are exceptionally high, ranging from 1000–2000 GM at 811.8 nm. Work on ruthenium-based TPA shows that enhancement could be achieved in coupled chromophores.<sup>14,15</sup> Humphrey *et al.* also have established that TPA cross sections are enhanced in Rualkynyl dendrimers and in Ru-capped ligand chains.<sup>17,18</sup> Based on these findings, we suggest that one way forward would be to develop W-centered dendrimers or W-based templates for ligand addition.

## Conflicts of interest

There are no conflicts to declare.

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