An investigation on the two-photon absorption activity of various terpyridines and related homoleptic and heteroleptic cationic Zn(II) complexes

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The two-photon absorption (TPA) properties of various terpyridines of the kind [4′-(C_6H_4-*p*-X)-2,2′:6′,2″-terpyridine] and related homoleptic and heteroleptic bis(terpyridine) cationic zinc(II) complexes were investigated by the TPA induced photoluminescence (TPA-PL) method in a femtosecond regime. It appeared that terpyridines bearing an X donor group are characterized by TPA cross sections among the largest ever reported for a molecule with a dipole symmetry whereas coordination to a Zn(II) center leads to a decrease of the TPA response.

1. Introduction

Molecular nonresonant two-photon absorption (TPA) has attracted growing interest over recent years due to the many applications it offers both in material science and in biological imaging.[1] For this reason, molecular engineering directed towards TPA optimization has become very active, leading to a range of molecules of various symmetries including dipoles,[2] quadrupoles,[3] octupoles,[4] and branched structures.[5] Most dipolar chromophores exhibit a smaller two-photon absorption cross-section in comparison with some quadrupolar and octupolar derivatives. However, combining dipolar branches within a three-branched octupolar structure can induce a very intense TPA response.[1f] Therefore there is a need for new dipolar chromophores with relatively high TPA ability. Although various electron-withdrawing heterocyclic moieties such as triazole,[1d] pyridine,[2] pyridinium,[5f] oxadiazoles,[5a,b] benzothiazole[6a] and benzothiadiazole[6b] have been used in the design of TPA active compounds, more extended heterocyclic moieties such as phenanthrolines have been investigated only recently by Prasad *et al.*[7] These authors showed that 1,10-phenanthrolines-containing π-conjugated chromophores with electron donor substituents such as a dihexylamino group are characterized by particularly large TPA cross-section values. In addition, when these chromophores coordinate with a metal center such as the nickel(II) ion, the resulting complexes do not lose their excellent TPA ability, the nickel(II) chelated complexes displaying red-shifted TPA bands compared with their metal-ion free chromophores.[7] This study, which can be considered a springboard to the design of coordination compounds with TPA properties which has been largely limited up to now to organic compounds, prompted us to investigate the TPA properties of other π-delocalized nitrogen donor ligands such as terpyridines and related zinc(II) complexes. In order to evaluate TPA cross section (δ) values, we used the TPA induced photoluminescence (TPA-PL) method[8] in a femtosecond regime. This helps reduce excited-state absorption events which can lead to artificially enhanced effective TPA cross-section values when nanosecond pulses are used.[1d,e]

2. Results and discussion

Various terpyridines bearing an electron donor or electron withdrawing substituent X of the kind [4′-(C_6H_4-*p*-X)-2,2′:6′,2″-terpyridine] [X = NBu_2 (**T_{D1}**), $N(C_{16}H_{33})_2$ (**T_{D2}**), *trans*-CH=CH(C_6H_4)-*p*-$N(C_{16}H_{33})_2$ (**T_{D3}**), CH_3 (**T_{D4}**), NO_2 (**T_A**); see Fig. 1] were prepared along with related novel cationic Zn(II) complexes [**T_{D3}**-Zn-**T_{D3}**][PF_6]$_2$ (**Zn1**), [**T_{D3}**-Zn-**T_{D4}**][PF_6]$_2$ (**Zn2**) and [**T_{D3}**-Zn-**T_A**][PF_6]$_2$ (**Zn3**) (see Experimental).

Their photophysical and TPA characteristics are shown in Table 1 whereas typical absorption and fluorescence emission spectra are shown in Fig. 2.

The TPA induced photoluminescence (TPA-PL) method requires luminescent compounds with a reasonable photoluminescence quantum efficiency (Φ_F), generally larger than 0.10, in order to obtain reliable TPA cross-section values. By choosing THF as solvent, Φ_F values in the range 0.33–0.66 were obtained for terpyridines **T_{D1}**, **T_{D2}**, and **T_{D3}** whereas that for complex [**T_{D3}**-Zn-**T_{D3}**][PF_6]$_2$ was 0.06 only. However, the use of acetone or DMF as solvent afforded adequate Φ_F values (0.44–0.50) for the various Zn(II) complexes. All these compounds exhibit large Stokes shifts, indicating that significant nuclear reorganization takes place after excitation prior to emission.[1d] The TPA-cross sections values are evidenced in Table 1 and Fig. 3. The TPA response of terpyridines **T_{D4}** and **T_A** could not be determined because their $\lambda_{\text{max, absorption}}$ is too low (280 nm).

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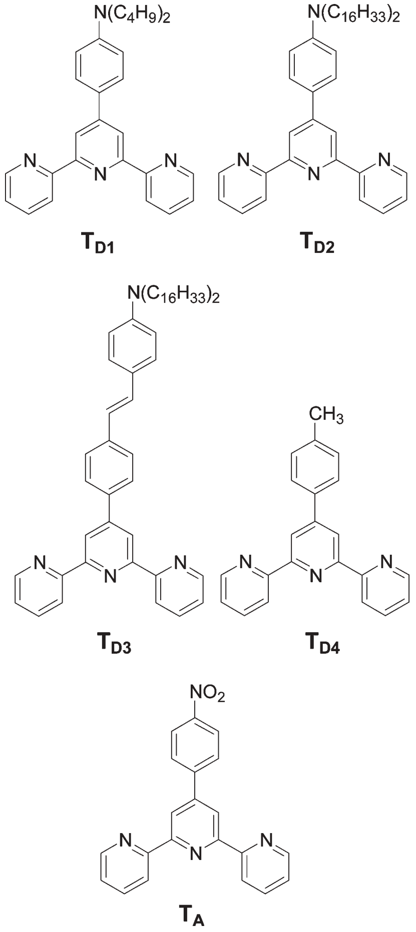


Fig. 1 Terpyridines investigated.

The TPA cross-section values for free ligands are remarkably high for simple dipolar molecules (87, 76 and 105 GM for $\mathbf{T_{D1}}$, $\mathbf{T_{D2}}$, and $\mathbf{T_{D3}}$ respectively, at 720 or 815 nm) when compared to that of AF-50 (δ = 22 GM at 796 nm),[1e] which has one of the largest δ values so far observed for a D–π–A structure and is usually referred as a TPA benchmark for 800 nm measurements.[1d,5f] The δ values are similar for $\mathbf{T_{D1}}$ and $\mathbf{T_{D2}}$ which differ only by the length of the alkyl chains on the donor amino substituent whereas the δ value of the more π-delocalized terpyridine $\mathbf{T_{D3}}$ is higher and the TPA band red-shifted with respect to $\mathbf{T_{D1}}$ and $\mathbf{T_{D2}}$ (Fig. 3). Such a trend is expected since it is commonly known that the increase of the conjugation length leads to an increase of the TPA activity.[3b,5f] Coordination to a cationic Zn(II) center leads to a decrease of the TPA response, the homoleptic complex [$\mathbf{T_{D3}}$-Zn-$\mathbf{T_{D3}}$][PF$_6$]$_2$ (**Zn1**) showing a δ value of 95 GM (at 815 nm) which corresponds to about half that of two $\mathbf{T_{D3}}$ molecules. The heteroleptic complexes [$\mathbf{T_{D3}}$-Zn-$\mathbf{T_{D4}}$][PF$_6$]$_2$ (**Zn2**) and

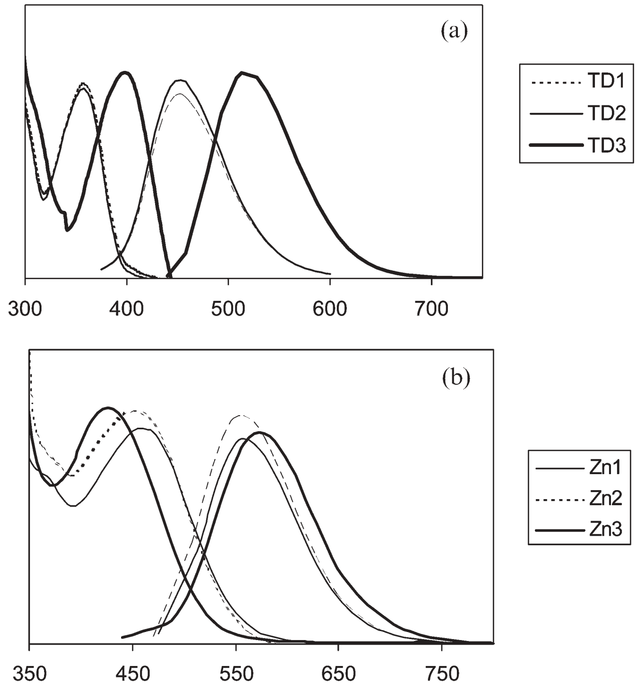


Fig. 2 (a) Normalized absorption and fluorescence emission spectra of free terpyridines. (b) Normalized absorption and fluorescence emission spectra of Zn(II) complexes.

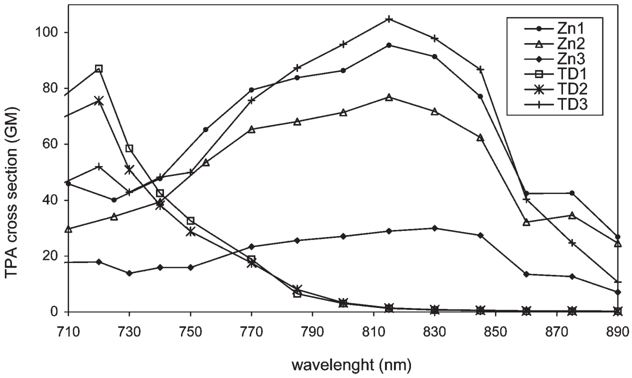


Fig. 3 Two-photon absorption for free terpyridines and Zn(II) complexes.

Table 1 Photophysical and TPA characteristics for various terpridines and related zinc complexes

Compound	Absorption λ_{max}/nm	Emission λ_{max}/nm	Φ_F[a]	Stokes shift/cm^{-1}[b]	TPA $\lambda^{(2)}_{max}$/nm	TPA cross-section δ /GM[c]
$\mathbf{T_{D1}}$	358[d]	453[d]	0.39	5900	720	87
$\mathbf{T_{D2}}$	356[d]	452[d]	0.33	6000	720	76
$\mathbf{T_{D3}}$	399[d]	516[d]	0.66	5700	815	105
Zn1	459[e]	576[e,f]	0.44	4400	815	95
Zn2	453[e]	577[e]	0.46	4700	815	77
Zn3	426[g]	576[g]	0.50	6100	830	30

[a] Fluorescence quantum yield, determined at room temperature with fluorescein (Φ_F = 0.92 in H$_2$O) as a reference. [b] Stokes shift: $1/\lambda_{abs}-1/\lambda_{em}$. [c] 1 GM (Goppert–Mayer) = 1 × 10^{-50} cm^4 s photon^{-1} molecule^{-1}. [d] In THF. [e] In acetone. [f] In THF, $\lambda_{max,\ absorption}$ and $\lambda_{max,\ emission}$ = 331 and 528 nm, respectively, and Φ_F = 0.06. [g] In DMF; in acetone, $\lambda_{max,\ absorption}$ and $\lambda_{max,\ emission}$ = 462 and 558 nm, respectively, and Φ_F = 0.01.

$[\mathbf{T_{D3}}\text{-Zn-}\mathbf{T_A}][\mathrm{PF_6}]_2$ (**Zn3**) have even lower values (77 GM at 815 nm and 30 GM at 830 nm, respectively). We note a considerably smaller δ value of $[\mathbf{T_{D3}}\text{-Zn-}\mathbf{T_A}][\mathrm{PF_6}]_2$ with respect to that of $[\mathbf{T_{D3}}\text{-Zn-}\mathbf{T_{D3}}][\mathrm{PF_6}]_2$ suggesting that, like for organic compounds, dipolar coordination complexes are less TPA active than multipolar ones. A decrease (of *ca.* 20%) in the TPA cross-section value was previously reported upon coordination to Ni(II) of two phenantrolines bearing a strong electron-donating group such as a dialkylamino group whereas an enhance TPA response was observed upon coordination to Ni(II) of phenanthrolines with weaker electron donors such as alkyloxy and alkylthio groups.

Clearly, the effect of coordination to a metal center on the TPA cross section of push–pull dipolar π-delocalized nitrogen donor ligands deserves more investigations. However, it is interesting to point out that the efficiency of push–pull dipolar (D–π–A) systems has been described by a very simple two-form two-state (2F2S) model developed by Barzoukas and Blanchard-Desce.[9] In this 2F2S model the electronic properties of the push–pull molecular system are described starting from two limiting electronic states: a neutral (D–π–A) and a charge transfer (D^+–π–A^-) one. The real electronic states of the molecule are a mixture of the two limiting forms, and the degree of mixing is specified by an empirical parameter MIX. The TPA cross section is a symmetric function of the MIX parameter, and shows a maximum efficiency for MIX values approximately half-way between those of the neutral or charge transfer form and the "cyanine" (*i.e.*, 50% weight for the neutral and charge transfer form) limit.[9] The above 2F2S model could explain the behaviour observed in the TPA spectra of the coordination compounds investigated here. Since coordination to a Zn(II) center leads to increased acceptor properties of the terpyridine rings of push–pull dipolar ligands such as T_{D1} and T_{D2},[10e] it reasonably modifies the weight of the neutral and charge transfer form affecting the ground electronic state, moving towards the "cyanine" structure, in agreement with the observed decrease of the TPA cross section. When the complex of Zn(II) with two terpyridine ligands is formed, if we consider that the electronic state of Zn(II) does not mix with the one of the ligands, the interaction between the ligands will be just a through space interaction. Because of the geometrical form of the coordination compounds, the two ligands are quite far apart and their interactions will be extremely weak. So it is likely that cooperative interactions will be negligible. Therefore the coordination compounds with two terpyridine ligands will have a TPA cross section which is the sum of the TPA cross section of the two single ligands but bound to the Zn(II) cation, characterized both by a lower TPA cross section than the one of the pure ligand.

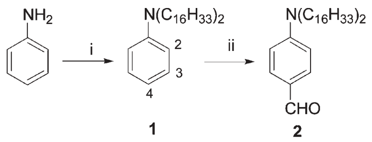
3. Conclusion

In conclusion, this study provides evidence of the remarkably high TPA activity of dipolar terpyridines bearing a donor substituent, which appear as very attractive building blocks for the design of TPA chromophores with practical applications. For example, combining dipolar branches of terpyridines within a three-branched octupolar structure is expected to give a very strong TPA response.[1f] In the case of two-photon excited fluorescence microscopy, high-performance fluorophores must exhibit both high fluorescence quantum yields (Φ) and large TPA cross-sections in the red–NIR range (700–1200 nm), corresponding to the biological optimal window for reduced photodamage.[4c] These requirements are fulfilled by the family of terpyridines investigated. Besides, it appeared that coordination to a Zn(II) metal center of these terpyridines leads to some decrease of the TPA response, an observation that can be explained by the 2F2S model.[9]

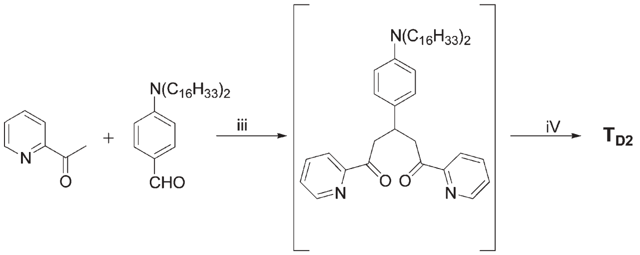
4. Experimental

Hexadecylbromide, K_2CO_3, KI, $POCl_3$, ^{t}BuOK, NH_4PF_6, CH_3OH, EtOH, CH_2Cl_2, anhydrous dimethylacetamide and DMF (on molecular sieves), $Zn(CH_3CO_2)_2\cdot 2H_2O$ and terpyridine T_{D4} were purchased from Sigma-Aldrich and used without further purification. Terpyridines $\mathbf{T_{D1}}$ and $\mathbf{T_A}$ were synthesized as already reported[10] while $\mathbf{T_{D2}}$ and $\mathbf{T_{D3}}$ were prepared as reported in Scheme 1 under nitrogen atmosphere, using flasks that were previously dried over flame and cooled under nitrogen flow. The novel zinc terpyridine complexes were prepared as reported below, following a procedure reported for similar complexes.[11]

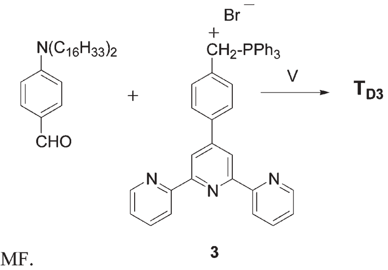
Products were characterized by ^{1}H-NMR (Bruker DRX-300 and 400 spectrometers) and UV–visible (Jasco V-530 spectrophotometer) spectroscopy, in some cases mass spectrometry (Varian VG9090 spectrometer) and elemental analysis which



i) $C_{16}H_{33}Br$, K_2CO_3, KI, DMA; ii) $POCl_3$, DMF.



iii) ^{t}BuOK, THF; iV) THF/EtOH, AcONH4



V) ^{t}BuOK, DMF.

Scheme 1 Synthesis of $\mathbf{T_{D2}}$ and $\mathbf{T_{D3}}$. (i) $C_{16}H_{33}Br$, K_2CO_3, KI, DMA; (ii) $POCl_3$, DMF. (iii) ^{t}BuOK, THF; (iv) THF–EtOH, $AcONH_4$. (v) ^{t}BuOK, DMF.

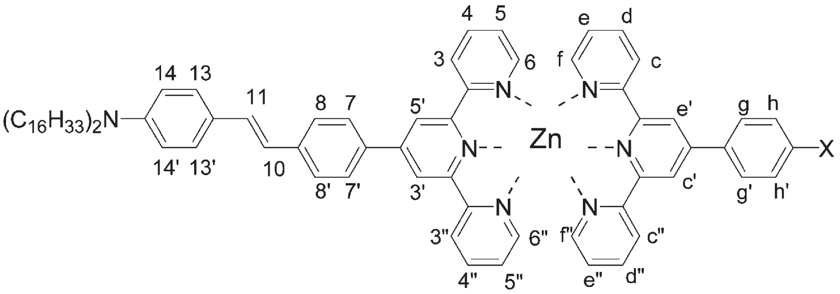


Fig. 4 Numbering for ^{1}H NMR spectra.

were carried out at the Dipartimento di Chimica Inorganica, Metallorganica ed Analitica of the Università di Milano.

For the numbering used in the attribution of the ^{1}H-NMR signals, see Fig. 4.

Two-photon absorption (TPA) spectra of the compounds studied were measured using TPA photoluminescence (TPA PL) spectroscopy.[8] Luminescence was excited *via* TPA by directing tightly collimated (~120 μm in diameter), high-intensity laser beam on a sample placed in a square spectroscopic cell. The emission was collected at 90° angle by a high numerical aperture lens and directed to a spectrometer's entrance slit through IR-blocking filters. The radiation dispersed by the spectrometer was detected by a thermoelectrically cooled CCD camera (Roper Scientific PIXIS 10:400). Excitation pulses with typical duration of 90 fs and maximum energy of approximately 6 nJ were produced by the mode-locked Ti:sapphire laser (Spectraphysics Tsunami) with repetition rate of 80 MHz. The laser's wavelength was tuned continuously within the spectral range 690–1000 nm. Neutral density filter wheel was used to attenuate the energy of the laser pulses down to desirable level.

TPA PL technique requires the use of a reference sample with known TPA cross-section spectrum and fluorescence quantum yield. In our experiments, we utilized 10^{-5} M aqueous solution of fluorescein (pH = 11). TPA cross-section spectra of fluorescein were taken from the literature,[12] and its fluorescence quantum yield was measured using an integrating sphere ($\Phi_F = 0.92$). Technical grade fluorescein was purchased from Acros Organics and used without purification.

Synthesis of terpyridines

The preparation of $\mathbf{T_{D2}}$ and $\mathbf{T_{D3}}$ required *N*,*N*-dihexadecylphenylamine (**1**) and 4-(*N*,*N*-dihexadecylamino)benzaldehyde (**2**) as reagents (Scheme 1) which preparation is reported below.

***N*,*N*-dihexadecylphenylamine (1).** Hexadecylbromide (15.2 mL, 50 mmol), K_2CO_3 (15.4 g, 110 mmol) and KI (1.32 g, 8 mmol) were added to a solution of aniline (1.96 mL, 22 mmol) in dimethylacetamide (80 mL) and the reaction mixture was stirred at 160 °C for 16 h. Removal of the solvent under vacuum afforded a thick residue, which was taken up with H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was dried over Na_2SO_4, affording a light brown wax. Purification by column chromatography on silica (hexane : Et_2O = 95 : 5) led to 9.1 g of **1** (76%) as a white solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 7.19 (dd, 2H, J = 7.0 Hz, J = 7.2 Hz, H_3, $H_{3'}$), 6.61 (m, 3H, H_2, $H_{2'}$, H_4), 3.23 (t, 4H, J = 7.4 Hz, N–CH_2), 1.56 (m, 4H, N–CH_2–CH_2–CH_2–), 1.28 (m, 52H, –CH_2), 0.87 (t, 6H, J = 6.8 Hz, CH_3). MS-FAB$^+$ *m*/*e* 542 $(M+H)^+$ (calcd for $C_{38}H_{71}N$ *m*/*e* 541). Anal. Calcd. (found): C, 84.21 (84.29); H, 13.20 (13.11); N, 2.59 (2.60).

4-(*N*,*N*-dihexadecylamino)benzaldehyde (2). Phosphoryl chloride (0.9 mL, 9.65 mmol) was added dropwise to anhydrous DMF (90 mL, 1.17 mol) at 0 °C under nitrogen flow. The mixture was stirred at 0 °C for 70 min, then at room temperature for 1 h. To the resulting yellow solution, heated at 95 °C, a solution of **1** (5.23 g, 9.65 mmol) in anhydrous DMF (50 mL) was added. The reaction mixture was stirred at 95 °C for 3 h. Removal of the solvent *in vacuo* afforded a thick residue, which was taken up with CH_2Cl_2 (50 mL) and washed several times with an aqueous satured solution of $NaHCO_3$, until pH was between 7 and 8. The organic layer was dried over $MgSO_4$ and evaporated. The brown solid thus obtained was purified by column chromatography on silica (hexane : Et_2O = 9 : 1), affording 3.14 g (57%) of **2** as a white waxy solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 9.70 (s, 1H, CHO), 7.70 (d, 2H, J = 8.8 Hz, H_3, $H_{3'}$), 6.66 (d, 2H, J = 8.8 Hz, H_2, $H_{2'}$), 3.32 (t, 4H, J = 7.3 Hz, N–CH_2), 1.61 (m, 4H, N–CH_2–CH_2–CH_2–), 1.30 (m, 52H, –CH_2), 0.87 (t, 6H, J = 6.6 Hz, CH_3). MS-EI *m*/*e* 569 (calcd for $C_{39}H_{71}NO$ *m*/*e* 569). Anal. Calcd. (found): C, 82.18 (82.63); H, 12.55 (12.98); N, 2.45 (2.46).

4′-[4-(*N*,*N*-dihexadecylamino)phenyl]-2,2′:6′,2″-terpyridine ($\mathbf{T_{D2}}$). 2-Acetylpyridine (0.43 mL, 3.86 mmol) was slowly added dropwise under nitrogen flow at room temperature to a suspension of ^{t}BuOK (0.668 g, 5.95 mmol) in anhydrous THF (20 mL) and the mixture was stirred at room temperature for 2 h. A solution of **2** (1.00 g, 1.75 mmol) in anhydrous THF (6 mL) was thus added. After stirring overnight, 95% aq. EtOH (30 mL) and solid $AcONH_4$ (4.7 g, 61.25 mmol) were added and the mixture refluxed for 4 h. The solvent was removed *in vacuo* and 10% aq. HCl (10 mL) was added, affording a red powder, which was filtered, dissolved in CH_2Cl_2 (50 mL) and washed with 10% aq NaOH, until pH was alkaline. The organic phase was dried over Na_2SO_4 and evaporated. The brown thick residue thus obtained was stirred with CH_3OH (10 mL), affording a yellow powder, which was purified by column chromatography on silica

(CH_2Cl_2 : CH_3OH : NH_3 = 100 : 10 : 1), leading to 550 mg (41%) of $\mathbf{T_{D2}}$ as a bright yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.73 (dd, 2H, J = 1.8 Hz, J = 5.0 Hz, H_6, $H_{6''}$), 8.70 (s, 2H, $H_{3'}$, $H_{5'}$), 8.66 (d, 2H, J = 7.9 Hz, H_3, $H_{3''}$), 7.86 (m, 4H, H_7, $H_{7'}$, H_4, $H_{4''}$), 7.33 (ddd, 2H, J = 1.2 Hz, J = 4.8 Hz, J = 6.0 Hz, H_5, $H_{5''}$), 6.72 (d, 2H, J = 9.0 Hz, H_8, $H_{8'}$), 3.32 (t, 4H, J = 7.0 Hz, N–CH_2), 1.62 (m, 4H, N–CH_2–CH_2–CH_2–), 1.26 (m, 52H, –CH_2), 0.87 (t, 6H, J = 6.2 Hz, CH_3). Anal. Calcd. (found): C, 82.33 (82.25); H, 10.43 (10.40); N, 7.24 (7.35).

4′-(4-{2-[4-(*N*,*N*-dihexadecylamino)phenyl]ethenyl}phenyl)-2,2′:6′,2″-terpyridine ($\mathbf{T_{D3}}$). Potassium *tert*-butoxide (0.169 g, 1.5 mmol) was added to a solution of 4-(2,2′:6′,2″-terpyridin-4′)-benzyl triphenyl phosphonium bromide **3** (0.500 g, 0.752 mmol), prepared as previously reported,[9e] in anhydrous DMF (18 mL). The dark red solution was stirred under nitrogen at room temperature for 45 min, then heated at 90 °C for 30 min, after which solid **2** (0.429 mg, 0.752 mmol) was added and the reaction mixture was stirred under nitrogen at 90 °C for 16 h. Removal of the solvent in vacuo afforded a thick residue which was taken up with CH_2Cl_2 (100 mL) and washed with H_2O (3 × 60 mL). The organic layer was dried over Na_2SO_4 and evaporated, to give a brown oily residue. This product was stirred with MeOH (10 mL) overnight, to afford 0.481 g of $\mathbf{T_{D3}}$ (73%) as a yellow–orange solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.78 (s, 2H, $H_{3'}$, $H_{5'}$), 8.76 (d, 2H, J = 4.5 Hz, H_6, $H_{6''}$), 8.70 (d, 2H, J = 7.9 Hz, H_3, $H_{3''}$), 7.90 (m, 4H, H_7, $H_{7'}$, H_4, $H_{4''}$), 7.62 (d, 2H, J = 8.1 Hz, H_8, $H_{8'}$), 7.43 (d, 2H, J = 8.3 Hz, H_{13}, $H_{13'}$), 7.37 (t, 2H, J = 6.5 Hz, H_5, $H_{5''}$), 7.15 (d, 1H, J_{trans} = 16.2 Hz, H_{10} o H_{11}), 6.95 (d, 1H, J_{trans} = 16.2 Hz, H_{10} o H_{11}), 6.65 (d, 2H, J = 8.3 Hz, H_{14}, $H_{14'}$), 3.32 (t, 4H, J = 7.0 Hz, N–CH_2), 1.62 (m, 4H, N–CH_2–CH_2–CH_2–), 1.28 (m, 52H, –CH_2), 0.90 (t, 6H, J = 6.8 Hz, CH_3). Anal. Calcd. (found): C, 83.63 (83.38); H, 9.90 (10.06); N, 6.90 (6.77).

Synthesis of complexes

[$\mathbf{T_{D3}}$-Zn-$\mathbf{T_{D3}}$][$\mathbf{PF_6}$]$_\mathbf{2}$. Solid $\mathbf{T_{D3}}$ (322.3 mg, 0.368 mmol) was added to a colorless solution of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (40.4 mg, 0.184 mmol) in CH_3OH (19 mL). The reaction mixture was stirred at room temperature for 30 min, then refluxed for further 30 min. To the red solution thus obtained, cooled at room temperature, a solution of NH_4PF_6 (66 mg, 0.405 mmol) in CH_3OH (5 mL) was added, leading to the immediate precipitation of a red solid. After 45 min of stirring at room temperature, it was collected and washed with a small amount of cool CH_3OH, leading to 287 mg (74%) of the desired complex as a red powder.

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.73 (s, 2H, $H_{3'}$, $H_{5'}$), 8.55 (d, 2H, J = 8.1 Hz, H_3, $H_{3''}$), 8.03 (d, 2H, J = 7.9 Hz, H_8, $H_{8'}$), 7.98 (t, 2H, J = 7.5 Hz, H_4, $H_{4''}$), 7.76 (d, 2H, J = 4.5 Hz, H_6, $H_{6''}$), 7.56 (d, 2H, J = 7.8 Hz, H_7, $H_{7'}$), 7.35 (m, 4H, H_{13}, $H_{13'}$, H_5, $H_{5''}$), 7.04 (d, 1H, J_{trans} = 15.9 Hz, H_{10} o H_{11}), 6.78 (d, 1H, J_{trans} = 15.9 Hz, H_{10} o H_{11}), 6.63 (d, 2H, J = 8.04 Hz, H_{14}, $H_{14'}$), 3.29 (m, 4H, N–CH_2), 1.61 (m, 4H, N–CH_2–CH_2–CH_2–), 1.29 (m, 52H, –CH_2), 0.90 (t, 6H, J = 6.4 Hz, CH_3). Anal. Calcd. (found): C, 69.58 (68.11); H, 8.23 (8.33); N, 5.32 (5.11).

[Zn($\mathbf{CH_3CO_2}$)$_\mathbf{2}$$\mathbf{T_{D3}}$]. Solid $\mathbf{T_{D3}}$ (90.2 mg, 0.103 mmol) was added to a colorless solution of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (22.6 mg, 0.103 mmol) in EtOH (25 mL). The reaction mixture was stirred at room temperature for 30 min, then refluxed for 1 h. Removal of the solvent under vacuum afforded 85 mg (78%) of the desired complex as an orange powder.

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.96 (d, 2H, J = 5.1 Hz, H_6, $H_{6''}$), 8.15 (s, 2H, $H_{3'}$, $H_{5'}$), 7.98 (d, 2H, J = 8.1 Hz, H_3, $H_{3''}$), 7.71 (t, 2H, J = 7.5 Hz, H_4, $H_{4''}$), 7.61 (d, 2H, J = 7.8 Hz, H_8, $H_{8'}$), 7.44 (m, 4H, H_{13}, $H_{13'}$, H_5, $H_{5''}$), 7.33 (d, 2H, J = 7.5 Hz, H_7, $H_{7'}$), 7.05 (d, 1H, J_{trans} = 16.2 Hz, H_{10} o H_{11}), 6.79 (d, 1H, J_{trans} = 16.2 Hz, H_{10} o H_{11}), 6.67 (d, 2H, J = 8.1 Hz, H_{14}, $H_{14'}$), 3.32 (t, 4H, J = 6.3 Hz, N–CH_2), 1.70 (m, 4H, N–CH_2–CH_2–CH_2–), 1.27 (m, 52H, –CH_2), 0.88 (t, 6H, J = 6.9 Hz, CH_3). Anal. Calcd. (found): C, 73.73 (72.96); H, 8.76 (8.61); N, 5.29 (5.23).

[Zn($\mathbf{CH_3CO_2}$)$_\mathbf{2}$$\mathbf{T_{D4}}$]. A solution of $\mathbf{T_{D4}}$ (130 mg, 0.4 mmol) in EtOH (10 mL) was added to a colorless solution of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (87.8 mg, 0.4mmol) in EtOH (10 mL). The pale yellow reaction mixture was refluxed for 1 h. Removal of the solvent *in vacuo* afforded 167 mg (82%) of the desired complex as a white powder.

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 9.06 (d, 2H, J = 4.9 Hz, H_6, $H_{6''}$), 8.31 (s, 2H, $H_{3'}$, $H_{5'}$), 8.22 (d, 2H, J = 8.0 Hz, H_3, $H_{3''}$), 7.99 (dt, 2H, J = 1.6 Hz, J = 7.5 Hz, H_4, $H_{4''}$), 7.65 (d, 2H, J = 8.1 Hz, H_7, $H_{7'}$), 7.61 (dd, 2H, J = 5.1 Hz, J = 7.6 Hz, H_5, $H_{5''}$), 7.38 (d, 2H, J = 8.0 Hz, H_8, $H_{8'}$), 2.48 (s, 3H, CH_3), 1.98 (s, 6H, CH_3CO_2). Anal. Calcd. (found): C, 61.62 (61.54); H, 4.57 (4.96); N, 8.29 (8.13).

[$\mathbf{T_{D3}}$-Zn-$\mathbf{T_A}$][$\mathbf{PF_6}$]$_\mathbf{2}$. Solid $\mathbf{T_A}$ (39.1 mg, 0.11 mmol) was added to a refluxing solution of [$Zn(CH_3CO_2)_2$$\mathbf{T_{D3}}$] (116.7 mg, 0.11 mmol) in CH_3OH (15 mL). The resulting red mixture was refluxed for 45 min. After cooling at room temperature, a solution of NH_4PF_6 (50 mg, 0.30 mmol) in CH_3OH (5 mL) was added, leading to the immediate precipitation of a red solid. After 45 min of stirring at room temperature, it was collected and washed with a small amount of cool CH_3OH and H_2O. The red powder thus obtained was dissolved in CH_2Cl_2 (15 mL), filtering the insoluble excess of NH_4PF_6 and finally affording 135 mg (77%) of the desired complex as a red solid.

^{1}H-NMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ (ppm) 9.53 (s, 2H, $H_{c'}$, $H_{e'}$), 9.41 (s, 2H, $H_{3'}$, $H_{5'}$), 9.13 (m, 4H, H_3, $H_{3''}$, H_c, $H_{c''}$), 8.59 (s, 4H, H_g, $H_{g'}$, H_h, $H_{h'}$), 8.34 (m, 6H, H_4, $H_{4''}$, H_d, $H_{d''}$, H_8, $H_{8'}$), 8.24 (m, 4H, H_6, $H_{6''}$, H_f, $H_{f''}$), 7.90 (d, 2H, J = 8.3 Hz, H_7, $H_{7'}$), 7.57 (m, 4H, H_5, $H_{5''}$, H_e, $H_{e''}$), 7.52 (d, 2H, J = 8.6 Hz, H_{13}, $H_{13'}$), 7.41 (d, 1H, J_{trans} = 16.3 Hz, H_{10} o H_{11}), 7.14 (d, 1H, J_{trans} = 16.3 Hz, H_{10} o H_{11}), 6.77 (d, 2H, J = 8.7 Hz, H_{14}, $H_{14'}$), 3.42 (m, 4H, N–CH_2), 1.67 (m, 4H, N–CH_2–CH_2–), 1.29 (m, 52H, –CH_2), 0.89 (t, 6H, J = 7.0 Hz, CH_3). Anal. Calcd. (found): C, 62.13 (62.26); H, 6.80 (6.49); N, 7.61 (7.40).

[$\mathbf{T_{D3}}$-Zn-$\mathbf{T_{D4}}$][$\mathbf{PF_6}$]$_\mathbf{2}$. *Procedure 1.* A solution of $\mathbf{T_{D4}}$ (27.5 mg, 0.0852 mmol) in CH_3OH (5 mL) was added to a refluxing solution of [Zn(CH_3CO_2)$_2$$T_{D3}$] (90.2 mg, 0.0852 mmol) in CH_3OH (12 mL). The resulting dark orange mixture was refluxed for 15 min. After cooling at room temperature, a solution of NH_4PF_6 (30 mg, 0.184 mmol) in CH_3OH (3 mL) was added, leading to the immediate precipitation of a dark orange solid. After 45 min of stirring at room temperature, it was collected and washed with a small amount of cool CH_3OH, affording 100 mg (75%) of the desired complex as an orange solid.

Procedure 2. Solid $\mathbf{T_{D3}}$ (135 mg, 0.152 mmol) was added to a solution of [Zn(CH_3CO_2)$_2$$\mathbf{T_{D4}}$] (78 mg, 0.152 mmol) in CH_3OH (28 mL). The resulting orange mixture was stirred at room temperature for 30 min, then refluxed for 45 min. After cooling at room temperature, a solution of NH_4PF_6 (60 mg, 0.368 mmol) in CH_3OH (5 mL) was added, leading to the immediate precipitation of a red solid. After 45 min of stirring at room temperature, it was collected and washed with a small amount of cool CH_3OH and H_2O, affording 180 mg (75%) of the desired complex as a red solid.

^{1}H-NMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ (ppm) 9.41 (s, 2H, $H_{3'}$, $H_{5'}$), 9.38 (s, 2H, $H_{c'}$, $H_{e'}$), 9.12 (m, 4H, H_3, $H_{3''}$, H_c, $H_{c''}$), 8.27 (m, 12H, H_4, $H_{4''}$, H_6, $H_{6''}$, H_8, $H_{8'}$, H_d, $H_{d''}$, H_f, $H_{f''}$, H_g, $H_{g'}$), 7.89 (d, 2H, J = 8.1 Hz, H_7, $H_{7'}$), 7.58 (m, 4H, H_5, $H_{5''}$, H_e, $H_{e''}$), 7.52 (d, 2H, J = 8.6 Hz, H_{13}, $H_{13'}$), 7.41 (d, 1H, J_{trans} = 16.3 Hz, H_{10} o H_{11}), 7.14 (d, 1H, J_{trans} = 16.2 Hz, H_{10} o H_{11}), 6.77 (d, 2H, J = 8.6 Hz, H_{14}, $H_{14'}$), 3.42 (m, 4H, N–CH_2), 1.67 (m, 4H, N–CH_2–CH_2–), 1.29 (m, 52H, –CH_2), 0.89 (t, 6H, J = 7.0 Hz, CH_3). Anal. Calcd. (found): C, 64.15 (64.05); H, 6.68 (6.77); N, 6.31 (6.13).

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