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Modular Synthesis of Elongated Phosphonate Bipyridines

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The synthesis and the photophysical properties of a series of bpy-R_2 derivatives **L1**–**L3** (bpy = 2,2′-bipyridine, R represents the substitution at the 4- and 4′-positions of the bpy) are described. R includes phosphonic ester groups as precursors for potent phosphonate anchoring groups, which enable immobilization on transition metal oxide semiconductor surfaces for applications like dye-sensitized solar cells (DSSCs) or dye-sensitized photoelectrosynthesis cells (DSPECs). The ligands **L1**–**L3** differ in the length of conjugated linker units between bpy core and anchoring groups. Phenylene and triazole moieties serve as building blocks for linker elongation. The resulting adjustability of the distance between semiconductor and chromophore represents a viable route to improve cell efficiency, as it will allow tuning of charge carrier recombination and dye aggregation. Furthermore the photophysical studies of the free ligands reveal a pronounced effect of the aryl substitution. The solid-state structures of **L1** and **L2** are reported within this contribution, enabling the determination of distances between bipyridine nitrogen donor and anchoring group.

Introduction

Metal–organic photosensitizers or photocatalysts anchored to semiconductor (SC) surfaces find important utilisation in DSSCs or DSPECs (dye-sensitized solar cells or dye-sensitized photoelectrosynthesis cells).[1–5] In particular, polypyridyl metal complexes have received extensive attention. They succeeded in converting light to electrical or chemical energy with good efficiency in *n*-type as well as in *p*-type cells.[2,4] For *n*-type DSSCs, the advantages of Ru-polypyridyl complexes are well known, whereas for *p*-type DSSCs, their use is still in its infancy.[2] The application of e.g. Re- or Ru-polypyridyl complexes for photocatalytic CO_2 reduction or hydrogen evolution on *p*-type SCs like TaON or NiO seems very desirable.[3,4,6]

In order to further develop the application potential, it is necessary to tune the properties of the dye for a good light-harvesting ability and an effective directional electron transfer, to overcome fundamental obstacles like recombination processes and to prevent aggregation of the chromophores. For this aim, it is important to modify the linkage between the semiconductor and the sensitizer and to extend the π-conjugated system of the ligands.[7–10] Hence, peripheral substitution of the most commonly used original 2,2′-bipyridine ligand might be an auspicious concept. As anchoring groups, phosphonic acid derivatives have been shown to be chemically more stable than others, both on *n*-type SCs like TiO_2 and on *p*-type materials like NiO.[2,11–18] Methyl phosphonic acids display especially high affinities to these SCs. In a recently published article on hole injection dynamics of ruthenium polypyridyl complexes into NiO, it was suggested, that the –I effect of the carboxylic anchoring groups (without linkers between chromophore and NiO) might hinder hole injection.[19] The CH_2 spacer in methyl phosphonic acid might prevent such an effect, since the electronic interaction between the bipyridine and anchoring groups is significantly reduced by the CH_2 group between them.[20] It is noteworthy that phosphonic esters can also be used to modify TiO_2 or other inorganic substrates. Organic-soluble dialkyl phosphonates are useful coupling agent alternatives to phosphonic acids, which are often difficult to solubilize and must be generated under harsh conditions from the corresponding ester.[11,21–24]

To increase the distance of the dye from the semiconductor surface and thereby potentially increase the lifetime of the excited states and slow down unfavorable recombination, it is necessary to introduce linkers between the anchoring group and the ligand moiety. In studies of dyes attached through flexible saturated linkers, it has been observed that the electronic coupling is weakened, and that charge carrier injection rates slow down with increased bridge length.[7] For this reason, synthetic efforts to introduce rigid and aromatic linkers like phenyl groups have followed in this context. For instance, Galoppini et al. have shown that the extinction coefficient of pyrene increases and the long-wavelength absorbance is shifted to the red when it is attached to fully conjugated rods.[25] They also equipped Ru-bpy sensitizers with elongated linkers of this kind and immobilized them on TiO_2. Concerning charge carrier transport there

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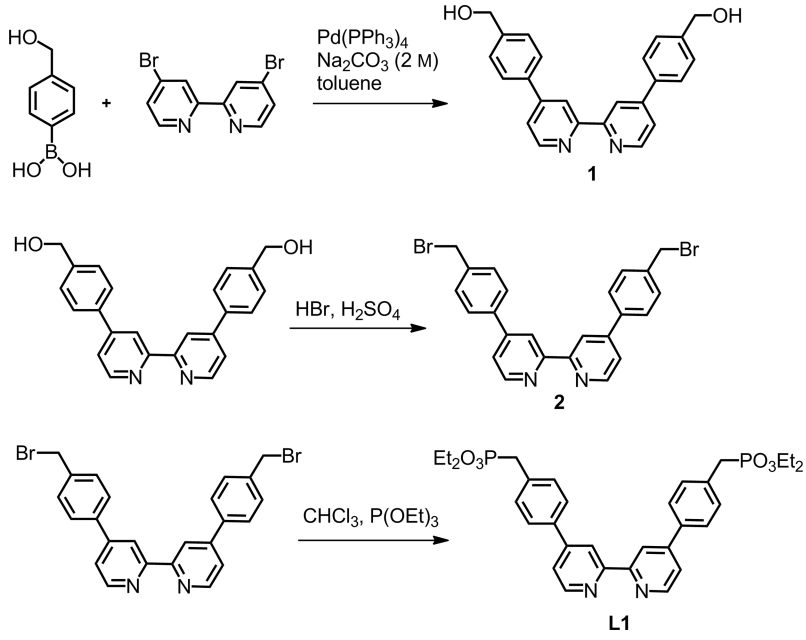
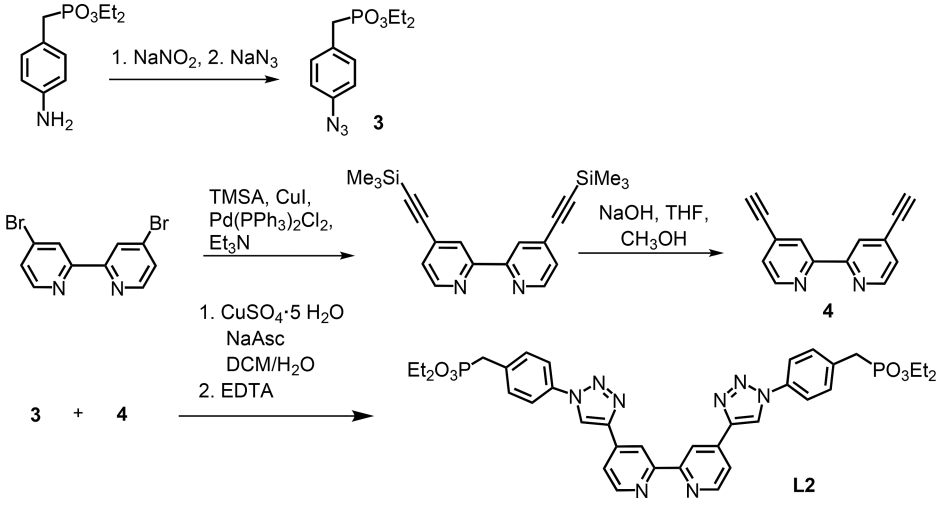
was only weak linker–length dependency.[26,27] They suggest that direct contacts of the Ru complex in the sponge-like environment of the mesoporous TiO_2 films may act as "short-circuits", highlighting the importance of anchoring group design. However, structure–property relationship studies for Ru-[($N^\wedge N$)$_2$($C^\wedge N$)]+ derivatives, where $N^\wedge N$ represents 2,2′-bipyridine, and $C^\wedge N$ represents bidentate phenylpyridine derivatives with carboxylate anchoring groups, were performed by Wu et al. for their application on NiO in *p*-type DSSCs. They differ in the number of phenylene spacer units between the Ru-[($N^\wedge N$)$_2$($C^\wedge N$)]$^+$ core and the anchoring group.[8] They found that as the number of the phenylene units in the linker increases, the interfacial charge recombination rate decreases, and the efficiency of the solar cells increases. Similarly, Nattestadt et al. increased the performance of *p*-type DSSCs by systematic variation of the distance between the hole in the NiO and a perylene monoimide (PMI) acceptor dye.[28] This might also be the case for molecularly sensitized semiconductors for photocatalytically active electrode materials in DSPECs, making distance control between semiconductor and sensitizer even more desirable, for example, to enhance the activity of an immobilized photocatalyst based on a hydrogen evolving photochemical molecular device.[29]

Generally, for a more chemically stable linkage between dye and semiconductor, both positions 4 and 4′ of the bpy should be equipped with anchoring groups. The superior chemical stability of phosphonate anchoring groups on transition metal oxide semiconductor surfaces should increase overall stability further.

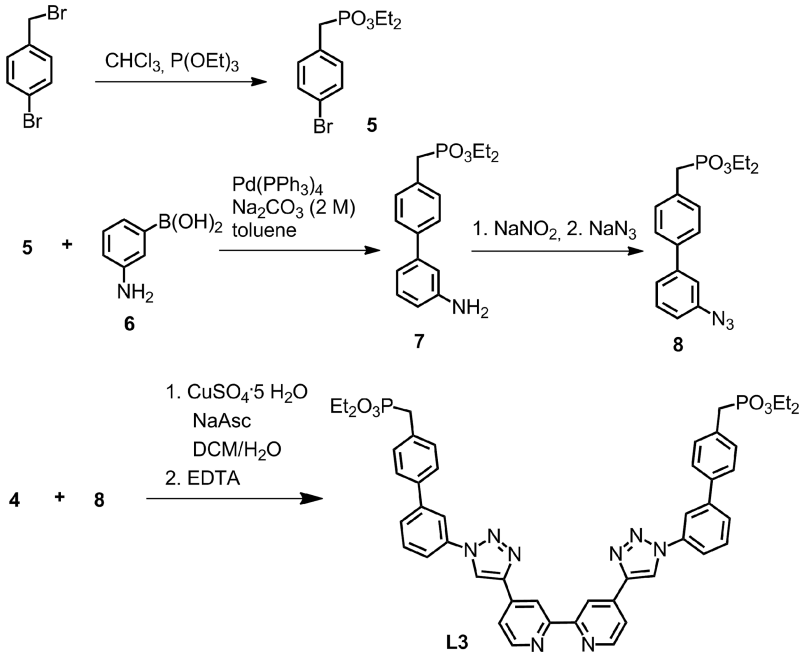
Taking all of this into consideration, we decided to develop strategies for the synthesis of 2,2′-bpy derivatives with



Scheme 1. Synthesis of ligand **L1**.



Scheme 2. Synthesis of ligand **L2**.



Scheme 3. Synthesis of ligand **L3**.

peripheral methyl phosphonic acid anchoring groups including aromatic linkers, such as phenylene and triazole units, for distance control in 4 and 4′-positions of the bpy (cf. Schemes 1, 2, and 3).

The phenylene group represents the archetype for a rigid and aromatic linker. Besides being aromatic and rigid units, triazoles can be synthesized by copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC, well-known under the general term of "click chemistry"). By definition, "click chemistry" is straightforward to perform under mild conditions, insensitive towards many functional groups, efficient and selective.[30]

With **L1**, **L2** and **L3** we have designed and synthesized three new bpy derivatives, which comprise the demands discussed above. Their phosphonic ester groups can easily be deprotected to generate the free acid functions, for their utilization as anchoring groups.[29,31,32]

Results and Discussion

Synthesis

The new bpy derivative **L1** has been prepared in three steps (cf. Scheme 1).

Suzuki coupling of (4-hydroxymethylphenyl)boronic acid with 4,4′-dibromo-2,2′-bipyridine gave compound **1** in 82% yield.[33] Compound **2** was then synthesized by substitution with hydrobromic acid in 73% yield.[31]

In the last step, the bromide groups of **2** could be substituted by phosphonic ester groups via the Arbuzov reaction with triethyl phosphite in 66% yield.[31] **L1** was characterized by ^{1}H, ^{13}C and ^{31}P NMR and high-resolution mass spectrometry (HRMS) (*m*/*z* (MALDI) = 609.22786). The structure was later confirmed by X-ray crystallography. A structurally closely related 6,6′-dimethyl-2,2′-bipyridine with phosphonic acid groups was reported by Housecroft et al. for its utilization as an anchoring ligand for copper(I) dyes in *n*-type DSSCs.[15] The presence of the phenylene spacer resulted in enhanced performances compared to dyes without this spacer between the bpy core and the phosphonic acid group. For this reason, we intended to get synthetic access to phosphonate bipyridine derivatives with even more aromatic spacer units. At first we tried to introduce another phenylene moiety, but the adaptation of numerous routes to prepare a suitable boronic acid coupling unit failed.[34–41] Therefore we inserted a triazole ring as an alternative since it is easy to generate via CuAAC (click) chemistry. This strategy allowed synthetic access to ligands **L2** and **L3** (cf. Scheme 2 and Scheme 3).

Azide **3** was generated from the corresponding amide (diethyl 4-aminobenzylphosphonate) using sodium nitrite and sodium azide (98% yield).[42] 4,4′-Bis(ethynyl)-2,2′-bipyridine (**4**) was prepared according to literature methods.[43] **L2** was synthesized by the click reaction between azide **3** and bipyridine **4** in 53% yield, with use of catalytic Cu^{II} in the presence of sodium ascorbate to generate Cu^{I} in situ.[44] **L2** was characterized by ^{1}H, ^{13}C and ^{31}P NMR, and HRMS [*m*/*z* (MALDI) = 743.26195.]. Additionally, crystals suitable for X-ray analysis were obtained.

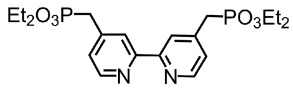
In order to insert more aromatic linkers between the bpy core and the anchoring unit by using bipyridine **4** and click chemistry, a new azide building block **8** needed to be generated. Compared to **3**, the distance between the azide group and the methylphosphonic ester group was increased by the introduction of another phenlyene unit via Suzuki coupling. The synthesis of **8** was accomplished in three steps (cf. Scheme 3).

First, compound **5** was prepared according to literature procedures (quantitative yield).[45] Then, Suzuki coupling of **5** and 3-aminophenylboronic acid (**6**) gave compound **7** in 97% yield. The solid-state structure of **7** was derived from X-ray suitable single crystals (Figure S1 in the Supporting Information). Finally, compound **8** was generated from **7** using sodium nitrite and sodium azide (quantitative yield).[42]

L3 was obtained by the click reaction of azide **8** and bisalkyne **4** in 30% yield, by using the same conditions as for the synthesis of **L2**.[44] The complexation of Cu^{I} with bipyridine might be one reason for the modest yield.[46] **L3** was characterized by ^{1}H, ^{13}C and ^{31}P NMR and HRMS [*m*/*z* (MALDI) = 895.32441].

Crystal Structures of L1 and L2

Solid-state structures of **L1**, **L2**, and the amine intermediate **7** of **L3** were obtained and compared to the known 4,4′-bis[diethyl(methylene)phosphonate]-2,2′-bipyridine (**L0**), where methylphosphonic ester groups are directly bound to the 4- and 4′-position of the bpy core, in the absence of aromatic linker units in between (cf. Figure 1).[29]



L0

Figure 1. Chemical structure of ligand **L0**.

Accordingly, the increase in length for the respective ligands can be compared directly from the values obtained. A direct characterization of the metal–surface distance of an immobilized complex depends on its binding mode towards the surface, which is unknown at this point. However, a comparative investigation of N–O3 distances was carried out, and is reflected in Table 1 along with characteristic values of bond lengths and angles of the methylenephosphonate moiety.

As proposed by Wu et al., a subsequent increase in anchor length may provide improved efficiencies for light-induced charge separation between a bipyridine-bound chromophore and an oxide surface.[8] The results from the solid-state structures show that the presented synthetic structures are a valuable approach in order to increase the length of a bipyridine with phosphonate anchors stepwise by about 3–4 Å per step. The overall distance between the metal-binding nitrogen of the bipyridine unit (N1) and the oxygen atoms of the phosphonic ester moiety (O3) increases from 5.5 Å for **L0** to approximately 15.8 Å for **L3** (Figure 2).

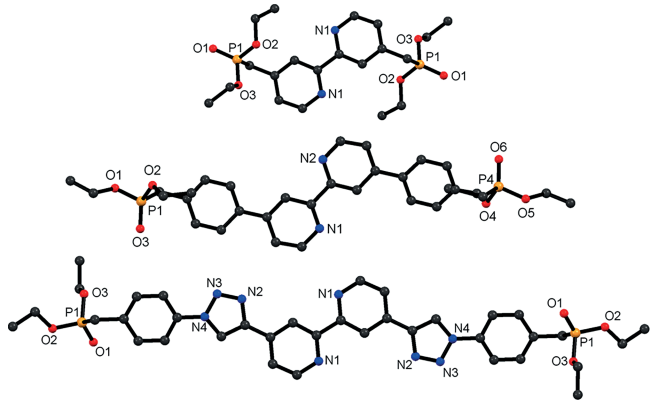


Figure 2. Solid-state structures of **L0**, **L1**, and **L2** (ball and stick depiction, hydrogen atoms omitted for clarity).

Photophysics

Absorption and emission spectra of the new bpy derivatives were measured in CH_2Cl_2 at a concentration of 7×10^{-5} M (Figure 3), and compared to **L0**. All three new ligands **L1**, **L2** and **L3** display broadened absorption bands relative to that of **L0**, together with a redshift of absorption behaviour. The absorption spectrum of **L0** features two distinct maxima at 285 and 250 nm, whereas for **L1**–**L3** only one maximum can be monitored. While the absorption maximum of **L1** is almost unchanged compared to the long-wavelength maximum of **L0**, a bathochromic shift to 293 nm and 297 nm is observed for the triazole-containing ligands **L2** and **L3**, respectively.

Bunz et al. compared photophysical properties of pyridine-containing 1,4-diaryltriazoles.[47] They found that photophysical properties were significantly influenced by the triazole moiety. This could be explained by resonance structures **I** and **II**, which offer an interpretation for the different photophysical properties in comparison to derivatives where no such mesomerism is accessible (cf. Figure 4). For **L2** and **L3**, these resonance structures might contribute to the red-shifted absorption maxima compared to **L0** and **L1**.

The influence of the elongated linker-system on the emission spectrum was obvious since it got more and more com-

Table 1. Characteristic lengths and angles.

Ligand	O3–N1[a] [Å]	PCH_2 [Å]	CH_2C$_{ar}$[b] [Å]	<PCH_2C$_{ar}$
L0[c]	5.562	1.791(1)	1.507(2)	115.7(1)°
L1[d]	9.807	1.794	1.509	112.0°
L2	12.935	1.793(3)	1.510(3)	114.1(2)°
L3	ca. 15.8[e]	1.788(2)	1.514(3)	112.2(1)°

[a] Distance between pyridine nitrogen atom and the calculated centroid centered between the phosphonate oxygen atoms. [b] Ar refers to aryl, i.e. either pyridyl or phenyl. [c] From ref.[17] [d] Median values from two molecules in the asymmetric unit. [e] Estimated value from the O3–N(amine) value of the intermediate structure **7** and the N(pyridine)–N(triazole) distance from **L2** (for details see Figure S4 in the Supporting Information).

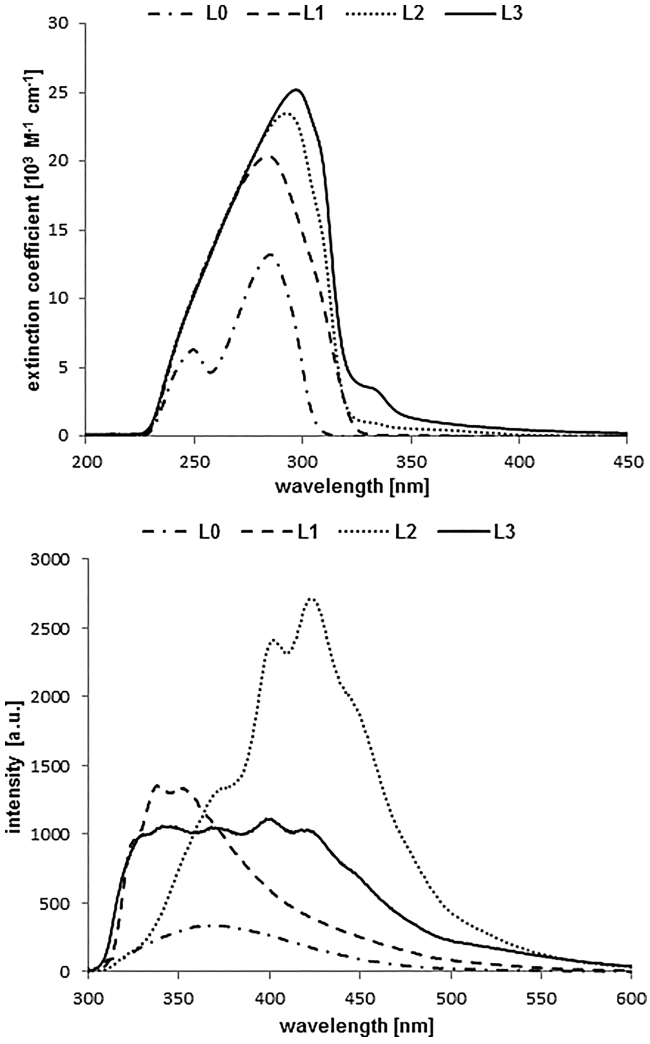


Figure 3. Absorption (top) and emission spectra (bottom) of ligands **L0**–**L3**.

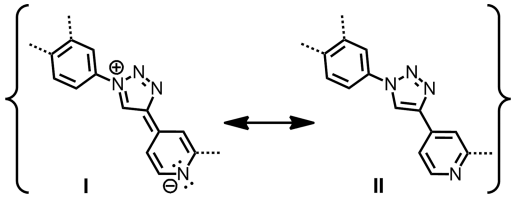


Figure 4. Resonance structures **I** and **II** of triazole-pyridines in **L2** and **L3**.

plex with increasing number of aromatic units from **L0** to **L3**. Generally, a broadening and a bathochromic shift of emission could be observed in this series. More aromatic substitution led to an increased number of individually distinguishable emission bands. The emission behavior of the azide building blocks **3** and **8** supports the assumption that electronic communication between the single aromatic units was hindered (Figure S32 and S33 in the Supporting Information). For **3** as well as for **8**, there was an emission band at around 375 nm. Compound **8**, with its two phenylene units, showed a second band at 422 nm, comparable with emission maxima of **L2** and **L3**. The existence of distinguishable emissive states speaks for weak electronic coupling within the single molecule moieties. This might be advantageous for the application of **L1**–**L3** in DSSCs or DSPECS, since charge carrier recombination should also be impaired.

For a more profound discussion of the luminescent behavior, theoretical calculations of the emissive states are necessary. Important absorption and emission features of **L0**–**L3** and building blocks **3** and **8** are summarized in Table 2.

Table 2. Absorption and emission data of ligands **L0**–**L3** and intermediates **3** and **8** measured in dichloromethane (absorption maxima λ_{abs}; emission maxima λ_{em}).

Substance	λ_{abs} [nm][a]	λ_{em} [nm]
L0	250 (6), 285 (13)	368
L1	285 (20)	326, 338, 353
L2	293 (23)	374, 402, 424, 445
L3	297 (25)	332, 345, 373, 400, 421
3	277 (3)	375
8	277 (6)	372, 422

[a] Extinction coefficient ($\varepsilon/10^3$ M^{-1} cm^{-1}) in brackets.

The absorption and emission data of **L1** to **L3** indicated that the substitution of the bipyridine frame with aromatic moieties resulted in significant changes in the electronic properties of the ligands.

Conclusions

Herein we presented a rational synthesis concept for increasing the distance between anchoring unit and bipydridine coordination sphere. We employed phenylene and triazole units as rigid and aromatic linkers to prepare elongated ligands **L1**–**L3** compared to the original 4,4′-bis[diethyl(methylene)phosphonate]-2,2′-bipyridine (**L0**). For **L1** and **L2**, this elongation was analyzed by X-ray crystallography and led to an increase in linker length from 5.5 Å to 15.8 Å. The vast potential of click chemistry should give versatile opportunities to employ different building blocks for tuning the extent of linkage and thereby the photophysical properties of bipyridines and their metal complexes. The photophysical studies in this contribution support the assumption that the linkers enhance the performance of chromophores or photocatalysts by shifting their absorption bathochromically. The elongated bipyridines might also slow down unfavorable recombination processes between semiconductor surfaces and photoactive units in DSSCs or DSPECs. The application of the ligands **L1**–**L3** in metal complexes and their effects on the performance of corresponding DSSCs and DSPECs, are currently under investigation.

Experimental Section

Methods and Materials: ^{1}H (400.13 MHz), ^{13}C NMR (101 MHz or 126 MHz) and ^{31}P (161.98 MHz) spectra were measured with a

Bruker DRX 400 or Bruker DRX 500 spectrometer. The NMR spectra were recorded in [D_6]DMSO or $CDCl_3$ at 298 K. ^{1}H-NMR and ^{13}C-NMR chemical shifts were referenced to the solvent peak for DMSO or chloroform.

MS analysis was performed with a Bruker solariX (2010) Hybrid 7T FT-ICR.

The crystal suitable for X-ray analysis was mounted using a MicroLoop and Fomblin oil. X-ray diffraction intensity data were measured at 180 K with a SuperNova (Dual Source) diffractometer, equipped with an ATLAS detector, from Agilent Technologies. The structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL 2013).[48] If not stated otherwise, the hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.

The UV/Vis-spectra were recorded with a JASCO Spectrometer V-670. Quartz cells with a 10 mm path length were used.

The emission spectra were recorded with a JASCO 25 Spectrofluorometer FP-8500. Quartz cells with a 10 mm path length were used.

If not mentioned otherwise, all experiments were performed under aerobic conditions.

Starting Materials: Starting materials were purchased from commercial sources and used without further purification.

Ligand Synthesis and Characterization

L0 was prepared according to literature procedures.[29]

4,4′-Bis(hydroxymethylphenyl)-2,2′-bipyridine (1): This compound was prepared by a modified literature procedure.[33] The reaction flask was charged with [4-(hydroxymethyl)phenyl]boronic acid (2 mmol, 304 mg), 4,4′-dibromo-2,2′-bipyridine (1 mmol, 314 mg), toluene (60 mL), and degassed aqueous sodium carbonate solution (2 M, 21 mL) under argon. Then the first portion of $Pd(PPh_3)_4$ (3 mol-% based on 4,4′-dibromo-2,2′-bipyridine, 35 mg) was added to the solution. After two days of boiling at reflux, a second portion of $Pd(PPh_3)_4$ (35 mg) was added, and the solution was heated to reflux for another 24 h. After the mixture cooled to room temperature, the toluene was evaporated. The crude product was washed sequentially with water, EtOH and Et_2O to give 4,4′-bis(hydroxymethylphenyl)-2,2′-bipyridine **(1)** in 82% yield (302 mg). Compound **1** shows poor solubility in both organic and aqueous solvents. ^{1}H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 8.73 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H), 8.67 (d, $^4J_{H,H}$ = 1.3 Hz, 2 H), 7.81 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H), 7.77 (dd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.8 Hz, 2 H), 7.48 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H), 5.30 (s, 2 H, O*H*), 4.56 (s, 4 H, CH_2-OH) ppm. HRMS (ESI): *m*/*z* calcd. for [M + H]$^+$ 369.15975; found 369.16046. IR (KBr): $\tilde{\nu}$ = 3344, 2119, 1027, 463 cm^{-1}.

4,4′-Bis(bromomethylphenyl)-2,2′-bipyridine (2): This compound was prepared by a modified literature procedure.[31] The bipyridine **1** (0.65 g, 1.76 mmol) was dissolved in a mixture of 48% HBr (165 mL) and concentrated sulfuric acid (61 mL). The resulting solution was refluxed for 6 h and then cooled to room temperature, and water (400 mL) was added. The pH was adjusted to neutral with conc. NH_3 solution, and the resulting precipitate was filtered and dissolved in $CHCl_3$. The solution was dried with magnesium sulfate, and the solvents were evaporated to dryness, yielding **2** (636.5 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.76 (d, $^3J_{H,H}$ = 5.1 Hz, 2 H), 8.73 (d, $^4J_{H,H}$ = 1.2 Hz, 2 H), 7.78 (d, $^3J_{H,H}$ = 8.3 Hz, 4 H), 7.57 (dd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.9 Hz, 2 H), 7.54 (d, $^3J_{H,H}$ = 8.3 Hz, 4 H), 4.56 (s, 4 H, CH_2-Br) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 67 °C): δ = 156.66, 149.77, 149.11, 139.15, 138.64, 129.93, 127.83, 121.84, 119.57, 32.71 ppm. HRMS (ESI): *m*/*z* calcd. for [M + 1H$^+$]$^+$ 494.98890; found 494.98931. IR (KBr): $\tilde{\nu}$ = 2957, 2922, 2852, 1592, 1539, 1456, 1359, 1261, 1226, 1196, 1097, 1021, 816, 727, 606 cm^{-1}.

L1: This compound was prepared by a modified literature procedure.[29] A chloroform (3 mL) solution of **2** (130 mg, 0.26 mmol) and triethyl phosphite (4 mL) was refluxed for 20 h under argon. The excess phosphite was removed under high vacuum. Flash chromatography using a 9:1 EtOAc/MeOH eluent gave the title compound as a white powder in 66% yield (105 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.74 (d, $^3J_{H,H}$ = 5.5 Hz, 2 H), 8.70 (d, $^4J_{H,H}$ = 1.3 Hz, 2 H), 7.75 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H), 7.55 (dd, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 1.8 Hz, 2 H), 7.44 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 2.4 Hz, 4 H), 4.09–3.99 [m, 8 H, PO(OCH_2CH$_3$)$_2$], 3.24 (d, $^2J_{H,P}$ = 21.8 Hz, 4 H, CH_2-PO_3Et_2), 1.26 [t, $^3J_{H,H}$ = 7.1 Hz, 12 H, PO(OCH$_2$CH_3)$_2$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 156.67, 149.62, 148.95, 136.88, 132.99, 130.50, 127.35, 121.62, 119.09, 62.29, 33.66 [d, ^1J (C,P) = 137.9 Hz], 16.52 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 25.88 ppm. HRMS (MALDI): *m*/*z* calcd. for [M + H]$^+$ 609.22779; found 609.22786. IR (KBr): $\tilde{\nu}$ = 3421, 2982, 2902, 1589, 1461, 1361, 1241, 1055, 1027, 965, 731, 707, 670, 604, 544 cm^{-1}. Crystals suitable for X-ray analysis were obtained by slow evaporation of chloroform.

Crystal Data for L1: $C_{32}H_{38}N_2O_6P_2$, M_r = 608.58 g mol^{-1}, colourless prism, crystal size 0.1945 × 0.1843 × 0.0979 mm^3, triclinic, space group $P\bar{1}$, a = 8.1949(2) Å, b = 19.3519(4) Å, c = 20.5664(5) Å, α = 107.877(2)°, β = 90.251(2)°, γ = 97.431(2)°, V = 3074.65(5) Å^3, T = 180(2) K, Z = 4, $\rho_{calcd.}$ = 1.315 Mg/m^3, μ (Cu-K_α) = 1.669 mm^{-1}, F(000) = 1288, altogether 31975 reflexes up to h(–9/10), k(–24/22), l(–25/21) measured in the range of 7.434° ≤ Θ ≤ 74.487°, completeness Θ_{max} = 99.7%, 12527 independent reflections, R_{int} = 0.0362, 10072 reflections with $F_o > 4\sigma(F_o)$, 757 parameters, 0 restraints, R_{1obs} = 0.0476, wR_{2obs} = 0.1341, R_{1all} = 0.0613, wR_{2all} = 0.1442, GOOF = 1.145, largest difference peak and hole: 0.783/–0.489 e Å^{-3}. CCDC-1400581 contains the supplementary crystallographic data for **L1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Diethyl 4-Azidobenzylphosphonate (3): This compound was prepared according to literature.[42]

4,4′-Bis(ethynyl)-2,2′-bipyridine (4): This compound was prepared according to literature.[43]

L2: This compound was prepared by a modified literature procedure.[44] Compound **3** (0.63 g, 2.34 mmol) was added to a solution of **4** (134 mg, 0.66 mmol) in CH_2Cl_2 (25 mL), which was followed by the addition of a mixture of copper sulfate pentahydrate (60 mg, 0.24 mmol) and (+)-sodium L-ascorbate (NaAsc; 117 mg, 0.59 mmol) in H_2O (25 mL). Upon the addition of the aqueous suspension to the orange organic phase, a black precipitate formed instantly. The mixture was stirred for 12 h and then poured into a saturated aqueous ethylenediaminetetraacetic acid (EDTA) solution (500 mL) and stirred for 14 h to remove Cu^{2+}. The resulting blue solution was extracted several times with $CHCl_3$. The combined organic extracts were dried with anhydrous $MgSO_4$, and the $CHCl_3$ was evaporated to afford the crude product. Flash chromatography using a 5:1 $CHCl_3$/MeOH eluent gave the title compound as a yellowish powder in 53% yield (258 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.84 (s, 2 H), 8.81 (d, $^3J_{H,H}$ = 5.1 Hz, 2 H), 8.57 (s, 2 H), 8.08 (dd, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 1.6 Hz, 2 H), 7.80 (s, 2 H), 7.78 (s, 2 H), 7.52 (dd, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 2.5 Hz, 4 H), 4.13–4.03 [m, 8 H, PO(OCH_2CH$_3$)$_2$], 3.24 (d, $^2J_{H,P}$ = 21.8 Hz, 4 H, CH_2-PO_3Et_2), 1.29 [t, $^3J_{H,H}$ = 7.1 Hz, 12 H, -PO(OCH$_2$-CH_3)$_2$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 156.50,

150.20, 146.27, 138.95, 133.43, 131.41, 120.74, 120.45, 119.65, 117.65, 62.51, 33.61 (d, $^1J_{C,P}$ = 137.9 Hz), 16.60 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 25.28 ppm. HRMS (MALDI): *m*/*z* calcd. for $[M + H]^+$ 743.26188; found 743.26195. IR (KBr): $\tilde{\nu}$ = 3445, 3115, 3085, 2984, 2907, 2114, 1605, 1519, 1416, 1387, 1249, 1031, 964, 858, 782, 717, 551 cm^{-1}. Crystals suitable for X-ray analysis were obtained by slow evaporation of chloroform.

Crystal Data for L2: $C_{36}H_{40}N_8O_6P_2$, M_r = 742.70 gmol^{-1}, yellow prism, crystal size 0.1121 × 0.0939 × 0.0288 mm^3, monoclinic, space group *P* 2$_1$/*n*, *a* = 8.5104(2) Å, *b* = 14.6092(3) Å, *c* = 15.2627(5) Å, β = 105.580(2)°, *V* = 1827.89(7) Å^3, *T* = 150(2) K, *Z* = 2, $\rho_{calcd.}$ = 1.557 Mg/m^3, μ (Cu-K_α) = 1.557 mm^{-1}, *F*(000) = 780, altogether 9020 reflexes up to *h*(–9/10), *k*(–18/13), *l*(–19/18) measured in the range of 7.497° ≤ Θ ≤ 74.491°, completeness Θ_{max} = 99.7%, 3724 independent reflections, R_{int} = 0.0190, 3217 reflections with $F_o > 4\sigma(F_o)$, 235 parameters, 0 restraints, R_{1obs} = 0.0536, wR_{2obs} = 0.1557, R_{1all} = 0.0612, wR_{2all} = 0.1650, GOOF = 1.055, largest difference peak and hole: 0.790/–0.527 e Å^{-3}. CCDC-1400582 contains the supplementary crystallographic data for **L2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Diethyl (4-Bromobenzyl)phosphonate (5): This compound was prepared according to literature.[45]

3′-Amino-4-diethyl(methylene)phosphonate-1,1′-biphenyl (7): The reaction flask was charged with 3-aminophenlyboronic acid (2.03 mmol, 315 mg), **5** (2.03 mmol, 624 mg), toluene (60 mL), and degassed aqueous sodium carbonate solution (2 M, 21 mL) under argon. Then the first portion of $Pd(PPh_3)_4$ (6 mol-% based on **5**) was added to the solution. After one day of boiling at reflux, a second portion of $Pd(PPh_3)_4$ (35 mg) was added, and the solution was heated to reflux for an additional 24 h. After the mixture cooled to room temperature, the toluene was evaporated. The crude product was extracted several times with CH_2Cl_2, and the combined organic extracts were dried with anhydrous $MgSO_4$. CH_2Cl_2 was evaporated, and the product was purified by flash chromatography using 9:1 EtOAc/MeOH as the eluent (630 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.38 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.22 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.3 Hz, 2 H), 7.05 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H), 6.82 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H), 6.75 (s, 1 H), 6.51 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.6 Hz, 1 H), 3.97–3.84 [m, 4 H, $PO(OCH_2CH_3)_2$], 3.06 (d, $^2J_{H,P}$ = 21.6 Hz, 2 H, CH_2-PO_3Et_2), 1.13 [t, $^3J_{H,H}$ = 7.1 Hz, 6 H, $PO(OCH_2CH_3)_2$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 146.70, 142.02, 139.99, 130.73, 130.13, 129.81, 127.30, 117.70, 114.30, 113.91, 62.33, 33.55 (d, $^1J_{C,P}$ = 138 Hz), 16.54 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 27.60 ppm. HRMS (ESI): *m*/*z* calcd. for $[M + H]^+$ 320.14101; found 320.14122. IR (KBr): $\tilde{\nu}$ = 3573, 2260, 1020, 668, 447 cm^{-1}. Crystals suitable for X-ray analysis were obtained by slow evaporation of chloroform.

Crystal Data for 7: $C_{17}H_{22}N_1O_3P_1$, M_r = 319.32 gmol^{-1}, colourless fragment, crystal size 0.3494 × 0.2048 × 0.1369 mm^3, monoclinic, space group $P\bar{1}$, *a* = 8.8460(4) Å, *b* = 9.9740(6) Å, *c* = 10.1215(5) Å, α = 109.307(5)°, β = 92.340(4)°, γ = 96.862(4)°, *V* = 833.68(8) Å^3, *T* = 150(2) K, *Z* = 2, $\rho_{calcd.}$ = 1.272 Mg/m^3, μ (Mo-K_α) = 0.177 mm^{-1}, *F*(000) = 340, altogether 10151 reflexes up to *h*(–10/11), *k*(–12/12), *l*(–12/12) measured in the range of 3.411° ≤ Θ ≤ 26.370°, completeness Θ_{max} = 99.7%, 3396 independent reflections, R_{int} = 0.0307, 2769 reflections with $F_o > 4\sigma(F_o)$, 206 parameters, 2 restraints, R_{1obs} = 0.0460, wR_{2obs} = 0.1065, R_{1all} = 0.0583, wR_{2all} = 0.1144, GOOF = 1.055, largest difference peak and hole: 0.407/–0.353 e Å^{-3}. CCDC-1400580 contains the supplementary crystallographic data for **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. General remarks: amine protons were assigned to appropriate electron density maxima, and their positions were fixed using the DFIX command. The N–H distance was chosen according to the default effective N–H distance as suggested following refinement with the TEMP command.

3′-Azido-4-diethyl(methylene)phosphonate-1,1′-biphenyl (8): This compound was prepared by a modified literature procedure.[42] Compound **7** (1.97 mmol, 630 mg) was dissolved in a mixture of water (15 mL) and concentrated hydrochloric acid (7.5 mL). The solution was cooled to 0 °C, $NaNO_2$ (338 mg, 4.90 mmol) in water (2 mL) were added, and the resulting solution was stirred for 45 min. Then NaN_3 (319 mg, 4.91 mmol) in water (2 mL) was added, and the reaction mixture was stirred for 1 h at 0 °C and 3.5 h at room temperature. The resulting solution was extracted several times with $CHCl_3$ and EtOAc. The combined organic extracts were dried with anhydrous $MgSO_4$, and the EtOAc was evaporated to afford the product **8** (681 mg, quantitative yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.45 (s, 1 H), 7.43 (s, 1 H), 7.35–7.26 (m, 4 H), 7.13 (t, $^4J_{H,H}$ = 1.8 Hz, 1 H), 6.93 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H), 4.04–3.91 [m, 4 H, $PO(OCH_2CH_3)_2$], 3.15 (d, *J* = 21.8 Hz, 2 H, CH_2-PO_3Et_2), 1.18 [t, $^3J_{H,H}$ = 7.1 Hz, 6 H, $PO(OCH_2CH_3)_2$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 142.64, 140.59, 138.87, 131.16, 130.44, 130.24, 127.36, 123.76, 117.89, 117.67, 62.64, 33.38 (d, $^1J_{C,P}$ = 138.4 Hz), 16.48 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 27.95 ppm. HRMS (ESI): *m*/*z* calcd. for $[M + H]^+$ 346.13150; found 346.13139. IR (KBr): $\tilde{\nu}$ = 2983, 2907, 2104, 1564, 1480, 1401, 1304, 1249, 1096, 1027, 962, 853, 784, 693, 604, 544 cm^{-1}.

L3: This compound was prepared by a modified literature procedure.[44] Compound **8** (0.70 g, 2.03 mmol) was added to a solution of **4** (178 mg, 0.87 mmol) in CH_2Cl_2 (30 mL), which was followed by the addition of a mixture of copper sulfate pentahydrate (80 mg, 0.32 mmol) and (+)-sodium (L)-ascorbate (NaAsc; 155 mg, 0.79 mmol) in H_2O (30 mL). Upon the addition of the aqueous suspension to the orange organic phase, a black precipitate formed instantly. The mixture was stirred for 12 h and then poured into a saturated aqueous ethylenediaminetetraacetic acid (EDTA) solution (600 mL) and stirred for 14 h to remove Cu^{2+}. The resulting blue solution was extracted several times with $CHCl_3$. The combined organic extracts were dried with anhydrous $MgSO_4$, and the $CHCl_3$ was evaporated to afford the crude product. Flash chromatography using 5:1 $CHCl_3$/MeOH as the eluent gave the product as a brownish oil with some impurities. This oil was diluted with $CHCl_3$, and title compound was obtained by precipitation with *n*-pentane as a brownish powder in 30% yield (235 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.81 (m, 4 H), 8.61 (s, 2 H), 8.08 (dd, $^3J_{H,H}$ = 5.0, $^4J_{H,H}$ = 1.7 Hz, 2 H), 8.04 (t, $^4J_{H,H}$ = 1.7 Hz, 2 H), 7.76 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H), 7.68 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H), 7.63 (m, 6 H), 7.44 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 2.4 Hz, 4 H), 4.10–4.02 [m, 8 H, $PO(OCH_2CH_3)_2$], 3.25 (d, $^2J_{H,P}$ = 21.8 Hz, 4 H, CH_2-PO_3Et_2), 1.28 [t, *J* = 7.1 Hz, 12 H, $PO(OCH_2CH_3)_2$] ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 156.47, 150.20, 146.27, 142.94, 138.94, 138.15, 137.36, 132.06, 130.64, 130.46, 127.76, 127.44, 120.44, 119.85, 119.26, 117.65, 62.36, 33.60 (d, $^1J_{C,P}$ = 138.3 Hz), 16.52 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 26.09 ppm. HRMS (MALDI): *m*/*z* calcd. for $[M + H]^+$ 895.32448; found 895.32441. IR (KBr): $\tilde{\nu}$ = 3350, 3282, 2923, 2852, 2334, 1868, 1739, 1233, 1022, 789, 717, 666, 545, 442 cm^{-1}.

Supporting Information (see footnote on the first page of this article): Experimental and characterization data, as well as additional figures.

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