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Full Paper

Layered γ-Zirconium Phosphate Intercalated with Ru(bpy)₃-Viologen Dyads as Unusual Materials for Dye-Sensitised Solar Cells: Improving Efficiency by Double Sensitisation

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The intercalation materials prepared from the laminar salt γ -zirconium phosphate and various dyads formed from Ru (bpy)₃ and viologens were tested as photoactive components in dye-sensitised solar cells. The efficiencies significantly increased, up to 0.2 %, when the materials were treated with the panchromatic N535 dye. A mechanism for this double sensitisation process is proposed, which should enable further improvement of these γ -ZrP-based materials as a reasonable alternative to the usual Ti-based dye-sensitised solar cells.

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Introduction

The versatile $(\gamma$ -ZrP) bears the molecular formula Zr(PO₄) $[O_2P(OH_2)] \cdot nH_2O$ and its lamellar structure (Fig. 1) was long ago refined by Rietveld methods from powder X-ray diffraction (XRD) patterns.^[1]

The structure reveals two kinds of phosphate groups. The non-acidic internal phosphate groups (green tetrahedrons) are the backbone of the layered structure, and remain bonded to four different Zr atoms. In contrast, the acidic surface phosphates (blue tetrahedrons) are responsible for the chemical properties of γ -ZrP. In short, this salt may enclose a wide variety of organic components in the interlayer space either by reaction with basic species leading to simple intercalation (ionic forces) or by topotactic exchange with organic phosphorous derivatives (covalent bonding).^[2] In the case of simple intercalation, the layered γ -ZrP acts as a surface of multiple negative counterions

of the various positively charged species, intercalated between the inorganic lamellae. The topotactic exchange is more complex because it involves the replacement of the surface phosphates by other phosphorous entities such as phosphonates. In this case, the phosphonates remain covalently linked to the inorganic layer and their degrees of freedom are much more limited.

The exploitation of these two processes, intercalation and topotactic exchange, using molecules with different structures and properties leads to a virtually unlimited number of solid materials with a broad range of features. Figure 2 shows a handful of examples of our own research.^[3]

In the future, it is expected that DSSCs will play a key role in ensuring the sustainability of energy conversion and/or production processes. To this effect, considerable research effort has been devoted to enhancing the efficiency of DSSCs based on



Fig. 1. Polyhedric structure of a layer of γ -zirconium phosphate, as deduced by powder X-ray diffraction.



Fig. 2. Summary of the main application areas of γ -ZrP-based materials, as explored by our research group.

titania, by far, the most used semiconductor in this area.^[4] Yet, despite these efforts, the maximum efficiency of titania-based DSSCs has seldom exceeded 10%, which is still too low for commercial use. Thus, it would be of prime interest in this context to explore alternative semiconducting materials. The aforementioned versatility of organic–inorganic hybrid materials based on γ -ZrP makes these substances worth examining in the DSSC field (Fig. 2, Path E).

Our recently performed laser flash-photolysis studies of γ -ZrP containing rather sophisticated arrangements of Ru(bpy)₃ and C60 derivatives^[5] suggested semiconducting properties of γ -ZrP that had not been contemplated before. Thus, we seriously considered the capabilities of laminar organic–inorganic γ -ZrP-based composites that have never been used for the construction of dye-sensitised solar cells (DSSCs).

As mentioned earlier, the beauty of γ -ZrP-based systems is that the photoactive ruthenium complexes (electron donors) and suitable electron acceptors (e.g. C60 or viologens) can be easily placed in their intergalleries to ensure a good interfacial contact between the photosensitive species and the semiconductor. Despite the relatively marginal efficiencies attained in our first attempts,^[6] we achieved a remarkable 20-fold improvement by covalently tethering the photoactive Ru complex and the acceptor species, and intercalation of the resulting dyad into γ -ZrP by very simple procedures.^[7] Although the best overall efficiency (0.1 %) of these materials was still well below the values currently achieved with titanium dioxide, we believe our work may pave the way to further research in layered organic–inorganic composites, the efficiency of which could be improved by the using a more suitable dye with a stronger and wider light absorption response and/or doping of the semiconducting salt.

In the present paper we address the issue by both modifying the structure of the Ru(bpy)₃-viologen dyads and adding a supplementary ruthenium dye (Ruthenizer 535 or N3), which has a wider panchromatic absorption range.

Results and Discussion

Scheme 1 shows the dyads and synthetic procedures used in the present study. The dyads were intercalated individually into γ -ZrP by routine procedures leading to the materials listed in Table 1.

Figure 3 shows models of the synthetised dyads 1–4. The measured interlayer distances by powder XRD are only compatible with an arrangement of the molecules aligning their longest axis parallel to the layers as shown in Fig. 4 for dyad 1. It should be noted that the lamellae are formed by two metal layers (Figs 1, 4). Therefore, two consecutive slabs containing 100 Zr atoms each enclose an interlayer space between two facing surfaces, each equivalent to the effective area surrounding 50 metal atoms. The available space as per Zr in the γ -ZrP



Scheme 1. Synthesis of dyads 1-4 (*i*: SeO₂, dioxane 110°C, 24h; *ii*: NaBH₄, MeOH, 3h; *iii*: PBr₃, CH₃CN, 3h; *iv*: bromide of (**A**), CH₃CN 90°C, 48h; *v*: Ru(bpy)₂Cl₂, ethanol : H₂O (1 : 1), 110°C; *vi*: lithium diisopropyl amide (LDA; 1 eq for dyads **2** and **3** or 2 eq for dyad **4**), THF -78°C, 1,3-dibromopropane (for dyads **2** and **4**) or 1,10-dibromodecane (for dyad **3**)). Dyad counterions were a mixture of chloride and bromide, which were lost in the intercalation (see text).

Table 1. Materials resulting from the intercalation of dyads 1-4 of Scheme 1 into γ-ZrP

 $(ZrPO_4)_{100} (H_{2-\alpha x}PO_4)_{100} (Dyad)_x (C_3H_6O)_z \cdot (H_2O)_w$

Material ^A	Elemental analysis ^B			Molecular formula			<i>d</i> ₁₀₀ [nm]
	C [%]	H [%]	N [%]	$(Dyad)_x$	Ζ	w/100	
$1 (\alpha = 4)$	20.0 (20.3)	3.6 (3.6)	2.4 (2.7)	(1) ₁₁	100	2	1.93
$2 (\alpha = 4)$	15.4 (15.1)	2.9 (2.8)	2.5 (3.0)	$(2)_{11}$	0	2.1	1.93
$3(\alpha = 4)$	17.0 (16.9)	3.2 (3.7)	1.7 (1.8)	(3) ₆	75	2	1.70
$4 (\alpha = 6)$	12.0 (11.9)	2.5 (2.6)	2.0 (2.2)	(4) ₆	0	2	1.64

 ${}^{A}\alpha$ denotes the number of positive charges of dyad or triad for computing the molecular formula.

^BData show found (calculated) values.

structure (Fig. 1) is $\sim 0.36 \text{ nm}^2$ or $50 \times 0.36 = 18 \text{ nm}^2$ for two consecutive lamellae containing 100 Zr atoms each. The models in Fig. 4 show that the projection area of dyads **1–3** is $\sim 1.7, 2.7$, and 3.5 nm², respectively. These simple considerations and the elemental analyses (Table 1) indicate that γ -ZrP was able to take in as much dyad as the available space allowed ($\sim 6-11$ dyads depending on the chain length). In the case of dyads **1** and **3**, some space remained that was occupied by acetone molecules from the intercalation medium. In the case of dyad **4**, a simple qualitative model (Fig. 3) indicates that the experimentally observed accommodation of six molecules per (50 + 50) Zr atoms (Table 1) requires some kind of cooperative arrangement. A similar situation would certainly be attained in the case of the other dyads.

The four resulting solid composites were deposited as thin films in order to build two sets of four corresponding cells. Scheme 2 shows the configuration of the cells used in the present study. Set A was assembled without further modification, whereas set **B** was prepared by additionally dipping the thin film into an ethanolic basic solution of N535 dye for 12h before their final assembly (see the Experimental section for details). Two additional cells were created from pristine γ -ZrP with and without N535 for comparison. It should be noted that it is unlikely that the N535 dye would reach the interlayer space of the particles because of the high occupation of this space by the dyads and the mild dipping conditions. No significant changes were observed between the powder X-ray patterns of the 'dipped' and 'non-dipped' films. Hydrogen bonding among the carboxylic acid groups and the particles outermost phosphates should allow the N535 dye to be easily adsorbed on the surface.

Table 2 summarises the results. The performance of the cells was evaluated by measuring the relevant parameters: opencircuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor (*FF*). The presence of co-sensitiser N535 did not significantly affect either the V_{oc} or *FF* values, whereas J_{sc} underwent a twoto-three fold increase in all cases studied. This behaviour was consistent in all the various studied replicas of the DSSCs sets, each of which was constructed independently. The observed general increment of J_{sc} can be explained in terms of the extra



Fig. 3. Molecular models of the dyads 1–3 (left) showing their calculated measurements and possible co-operative arrangement of the intercalated dyads 3–4 (right).



Fig. 4. Representative molecular model of two layers of γ -ZrP at the experimental interlayer distance containing the appropriate number of molecules of dyad 1, as deduced from elemental analysis.

photons absorbed by the panchromatic N535 co-sensitiser that should contribute to the increasing number of charge separation events. Interestingly, the overall efficiency of the cells containing the two photo-sensitisers, i.e. the ruthenium–viologen dyads in the intergallery space and the panchromatic N535 dye on the external surface of the laminar particles, reached similar values in the range of 0.15-0.18 %. The fact that the control cells, built from pristine γ -ZrP, showed low and similar efficiencies (0.04 % and 0.06 % for sets **A** and **B**, respectively) points to a synergistic effect between the interlayer dyads and the adsorbed N535 dye. The measured photoresponse of some of the devices (Fig. 5) supports this conclusion. Unusual materials for dye-sensitised solar cells



Scheme 2. General diagram of the γ -ZrP-based DSSCs assembled in this work.

Table 2.	Performance	of the t	wo sets	of DS	SCs pr	epared	with	the
γ-ZrP-bas	ed materials	1-4 upor	ı illumi	nation	with a	solar	simula	tor
	through	a 1.5 a.m	n. filter :	at 1000	Wm^{-}	2		

 $V_{\rm OC}$, voltage at open circuit; $J_{\rm SC}$, current density at short circuit; *FF*, fill factor.

Material (set) ^A	$V_{\rm oc} [{\rm mV}]$	$J_{\rm sc}$ [$\mu A {\rm cm}^{-2}$]	FF [%]	Efficiency [%]
γ -ZrP(A)	601.83	122.49	56.2	0.04
γ -ZrP(B)	595.41	174.74	56.6	0.06
1(A)	527.01	147.11	65.8	0.05
1(B)	574.19	484.84	66.3	0.18
2(A)	544.21	276.21	71.0	0.11
2(B)	550.90	419.19	65.2	0.15
3(A)	461.49	63.13	77.4	0.02
3(B)	538.59	427.85	66.8	0.15
4(A)	456.92	132.32	73.1	0.04
4(B)	546.14	475.01	62.9	0.16

^ASet A without N535; set B with N535 (see Scheme 2).

The highest photocurrent occurs at \sim 350 nm. In previous studies, we attributed this to direct light absorption by the inorganic matrix, the dyad thus being responsible for the less strong and discreet absorption at 475 and 690 nm. However, when the N535 dye is present, the current is much more effectively produced over a wider wavelength range, a finding that can explain the efficiency increase in set **B** cells (Table 2). A plausible explanation is illustrated in Scheme 3. When the N535 dye is present on the surface of the particles,^{\dagger} sensitisation should occur more effectively. All N535 molecules are readily exposed to the incoming light, whereas only a few of the dyads in the outermost layers could be excited. Our hypothesis is that the effective N535 light-harvesting molecules could transfer the absorbed energy to the ground state of the Ru(bpy)₃ end of the dyads that were not excited by the incident light. Therefore, the role of the surface N535 molecules would be that of an energy pump or conveyor belt, i.e. a kind of catalyst that makes the entire light-absorption process more effective. Once the dyad gets the energy from the N535 molecules, electron transfer to the viologen takes place in either an intra- or intermolecular



Fig. 5. Representative IPCE spectra for the cell built from **1** without (a) and with (b) N535 dye co-sensitisation.

fashion. The different performance of materials 1-3 (in the absence of the N535 dye) with diverse spacer lengths suggests that the intramolecular Ru(bpy)₃-to-viologen electron transfer is the favoured process. This was more pronounced with the fourmethylene spacer.

Following the dyad charge separation, electrons start being injected into the γ -ZrP semiconducting layers, resulting in the generation of the light-induced current. Figure 6 supports the semiconducting behaviour of γ -ZrP. The cyclic voltammetry of pure γ -ZrP (Fig. 6a) exhibited a reversible peak at -0.6 V, corresponding to the reduction of the material. The corresponding reduction peak in cyclic voltammetry supports the possibility that the charge-separated dyad can inject an electron into the γ -ZrP layered salt. In addition, if a thin film of γ -ZrP supported on fluorine-doped tin oxide (FTO) glass is subjected to a 0-V bias potential and the electrode is illuminated at 300 nm, a photocurrent of $\sim 0.5 \,\mu$ A can then be measured (see inset 1 of Fig. 6a), a fact that further reinforces the behaviour of layered γ -ZrP as a semiconductor. Finally, Kubelka–Munk optical

[†]The presence of the dyads or triad on the outer surface of the particles cannot be completely ruled out after the dipping process. Therefore, some dyads or triad and the N535 dye would be in closer contact at the particles surface. This is a possible option that has to be investigated further.



Scheme 3. Proposed mechanism for the energy transfer process in the doubly sensitised materials.

measurements (Fig. 6b) of pristine γ -ZrP revealed a band gap energy of 6.2 eV, which is surprisingly higher than expected.

In conclusion, the photovoltaic response observed for modified γ -ZrP and the outcome of the photo-electrochemical measurements for γ -ZrP have two important implications: (1) the absorption of light appears to be much more effective at the surface of the particles; and (2) the semiconducting properties of γ -ZrP are not very good because its bandgap is relatively high. Yet, the studies presented herein illustrate once more the high versatility offered by layered γ -ZrP in building composite materials, which definitely have potential for use in the solar cell field. For instance, although still quite preliminary, our very recent measurements of γ -ZrP containing 5–7% of Nb in the layers showed a reduced band gap of ~4.0 eV (Fig. 6b), 2.2 eV lower than that of pure γ -ZrP. The application of metal-doped γ -ZrP together with the co-sensitisation method described in this paper, the investigation of other photosensitising dyes, and a better control of the particle size would lead to a substantial improvement of γ -ZrP-based DSSCs, all of which are currently under investigation.

Experimental

Synthesis of Dyads 1-4

Preparation of 1-ethyl-4-pyridin-4-ylpyridinium bromide (**A**)

In a sealed tube, a mixture of 4,4'-bipyridine (5 g, 32.0 mmol) and bromoethane (2.6 mL, 32.0 mmol) was stirred at room temperature for 96 h, yielding a pale yellow solid that was filtered and washed with diethyl ether, toluene, and acetone. The remaining solid was dissolved in acetonitrile, and the solution was filtered and the solvent was evaporated. Yield



Fig. 6. (a) Cyclic voltammetry of γ -ZrP supported on FTO (i) and FTO substrate (ii) as reference in a 0.1 M LiClO₄ acetonitrile solution. Inset 1 shows the photocurrent measured for this thin film of γ -ZrP as a function of the excitation wavelength at 0-V bias potential. Inset 2 shows the photocurrent during repeated on/off cycles upon illumination with monochromatic light of 300 nm wavelength. (b) Tauc's graphs from Kubelka–Munk optical measurements of pristine γ -ZrP and of its 7 % Nb-doped counterpart.

(85 %). ¹H NMR (300 MHz, DMSO) δ (ppm): 1.57 (t, *J* 7.3, 3H), 4.71 (q, *J* 7.3, 2H), 8.05 (m, 4H), 8.65 (d, *J* 6.8, 2H), 8.84 (m, 2H), 9.31 (d, *J* 7.1, 2H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 16.29, 55.89, 121.85, 125.31, 140.82, 145.09, 150.87, 152.08.

Synthesis of 1-ethyl-1'-[(4'-methyl-2,2'-bipyridin-4-yl) methyl]-4,4'-bipyridinium dibromide (Bipy1-A)

A mixture of 4-(bromomethyl)-4'-methyl-2,2'-bipyridine^[8] (250 mg, 0.95 mmol), and **A** bromide (264 mg, 0.99 mmol) in CH₃CN (6.5 mL) was heated at 90°C for 120 h in a sealed tube. The resulting yellow precipitate was filtered off and washed with hot acetonitrile and diethyl ether, yielding 381 mg (73 %) of the product. ¹H NMR (300 MHz, CD₃OD) δ (ppm): 1.73 (t, *J* 7.4, 3H), 2.47 (s, 3H), 4.80 (q, *J* 7.4, 2H), 6.16 (s, 2H), 7.31 (d, *J* 5.0, 1H), 7.58 (dd, *J* 1.8, 5.0, 1H), 8.23 (m, 1H), 8.47 (d, *J* 5.0, 1H), 8.70 (d, *J* 6.8, 2H), 8.77 (m, 3H), 9.30 (d, *J* 6.8, 2H), 9.44 (d, *J* 7.0, 2H). ¹³C NMR (75.5 MHz, CD₃OD) δ (ppm): 16.71, 21.21, 58.85, 64.41, 121.47, 123.79, 124.43, 126.72, 128.46, 128.89, 144.69, 146.78, 146.95, 147.76, 150.01, 150.88, 151.63, 152.28, 156.08, 158.43.

Preparation of Dyad 1

A mixture of **Bipy1-A** (160 mg, 0.320 mmol) and *cis*-bis(2,2'bipyridine)dichlororuthenium (170 mg, 0.351 mmol) in ethanol : water (7 : 3, 11.8 mL) was heated at 110°C for 24 h, protected from ambient light. The mixture was concentrated under vacuum to yield a dark solid that was used to prepare 1 without further purification. ¹H NMR (300 MHz, CD₃OD) δ (ppm): 1.73 (t, *J* 7.2, 3H), 2.60 (s, 3H), 4.82 (q, *J* 7.2, 2H), 6.26 (s, 2H), 7.36 (d, *J* 6.4, 1H), 7.34–7.58 (m, 4H), 7.63 (d, *J* 5.7, 2H), 7.77–7.85 (m, 3H), 7.89 (d, *J* 6.0, 1H), 7.98 (d, *J* 4.9, 1H), 8.08–8.16 (m, 4H), 8.68–8.81 (m, 9H), 9.02 (s, 1H), 9.30 (d, *J* 7.2, 2H), 9.54 (d, *J* 7.2, 2H). ¹³C NMR (75.5 MHz, CD₃OD) δ (ppm): 16.71, 21.25, 58.50, 63.50, 125.57, 125.62, 125.69, 127.40, 128.48, 128.91, 128.97, 129.05, 129.14, 130.34, 139.15, 139.27, 144.70, 146.88, 147.98, 151.17, 151.71, 152.22, 152.27, 152.49, 152.70, 152.77, 153.14, 153.43, 157.36, 158.32, 158.47, 158.49, 158.53, 159.60.

Preparation of 4-(4-bromobutyl)-4'-methyl-2,2'bipyridine (Bipy2)

Butyllithium (1.6 M in hexane, 2.7 mL, 4.34 mmol) was added to a solution of diisopropylamine (0.61 mL, 4.34 mmol) in THF (9 mL) at -78° C. The mixture was stirred for 45 min and

solution of 4,4'-dimethyl-2,2'-bipyridine added to а (1 g, 5.43 mmol) in dry THF (38 mL) at -78° C. After 1 h, at 78°C, the resulting brown-red solution was treated with dibromopropane (0.88 mL, 8.69 mmol). After stirring for 1 h, a pale green colour developed. The mixture was allowed to reach room temperature for 3 h and the reaction was quenched with water. Phosphate buffer (1 M, 10 mL, pH 7.0) was added and the mixture was extracted with diethyl ether. Usual work-up of the organic layer yielded a crude product that was purified by silica gel chromatography with 1:1 ethyl ether: hexane, producing a colourless oil (0.69 g, 42 %). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.89 (m, 4H), 2.44 (s, 3H), 2.74 (t, J 7.3, 2H), 3.42 (t, J 6.6, 2H), 7.14 (d, J 1.4, 2H), 8.24 (s, 2H), 8.54 (d, J 5.2, H), 8.57 (d, J 5.1, H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 156.0, 156.0, 152.9, 148.9, 148.8, 148.1, 124.6, 123.9, 122.0, 121.3, 34.26, 33.01, 31.93, 28.51, 20.95.

Synthesis of 1-ethyl-1'-[4-(4'-methyl-2,2'-bipyridin-4-yl) butyl]-4,4'-bipyridinium dibromide (*Bipy2-A*)

A mixture of **Bipy2** (309 mg, 1.03 mmol) and **A** bromide (290 mg, 1.08 mmol) in CH₃CN (10 mL) was heated at 90°C for 48 h in a sealed tube. The resulting yellow precipitate was filtered off and washed with hot acetonitrile and diethyl ether, yielding 300 mg (52%) of the product. ¹H NMR (300 MHz, DMSO) δ (ppm): 1.60 (t, J7.4, 3H), 1.71 (m, 2H), 2.04 (m, 2H), 2.40 (s, 3H), 2.77 (t, J7.5, 2H), 4.74 (m, 4H), 7.29 (m, 2H), 8.22 (d, J7.1, 2H), 8.52 (dd, J4.8 Hz; 15.6, 2H), 8.78 (d, J4.9, 4H), 9.41 (d, J6.5, 4H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 16.27, 20.68, 26.21, 30.27, 33.80, 56.52, 60.58, 120.45, 121.21, 124.15, 124.89, 126.51, 126.61, 145.57, 145.73, 147.91, 148.48, 148.54, 148.90, 149.15, 151.46, 155.04, 155.30.

Preparation of Dyad 2

A mixture of **Bipy2-A** (300 mg, 0.526 mmol) and *cis*-bis (2,2'-bipyridine)dichlororuthenium (331 mg, 0.684 mmol) in ethanol: water (7:3, 24 mL) was heated at 110°C for 24 h protected from ambient light. The mixture was concentrated in vacuum to yield 631 mg of a dark solid that was used to prepare **2** without further purification. ¹H NMR (300 MHz, CD₃OD) δ (ppm): 1.73 (t, *J* 7.5, 3H), 1.92 (m, 2H), 2.24 (m, 2H), 2.59 (s, 3H), 2.97 (m, 2H), 4.85 (m, 4H), 7.32 (d, *J* 5.7, H), 7.41 (d, *J* 5.7, H), 7.44–7.56 (m, 4H), 7.59 (d, *J* 5.7, H), 7.64 (d, *J* 5.9, H), 7.78–7.87 (m, 4H), 8.07–8.17 (m, 4H), 8.65–8.75 (m, 10H),

9.28 (d, *J* 6.4, 2H), 9.34 (d, *J* 6.4, 2H). ¹³C NMR (75 MHz, CD₃OD) δ (ppm): 16.86, 21.32, 27.48, 31.87, 35.24, 58.64, 62.70, 125.66, 125.91, 126.70, 128.33, 128.87, 128.92, 128.98, 129.16, 129.78, 139.01, 146.81, 147.10, 151.11, 151.52, 151.85, 151.92, 152.49, 152.54, 155.07, 157.82, 158.09, 158.33, 158.37, 158.45.

Preparation of 4-(11-bromoundecyl)-4'-methyl-2,2'bipyridine (**Bipy3**)

Butyllithium (1 M in hexane, 2.17 mL, 2.17 mmol) was added to a solution of diisopropylamine (0.304 mL, 2.17 mmol) in THF (4.5 mL) at 78°C. The mixture was stirred for 45 min and added to a solution of 4,4'-dimethyl-2,2'-bipyridine (0.5 g, 2.71 mmol) in THF (19 mL) at -78° C. After 1 h at 78°C, the resulting brown-red solution was treated with 1,10-dibromodecane (1 mL, 4.34 mmol) and, after stirring for 1 h, a pale green colour was developed. The mixture was allowed to reach room temperature for 3 h and the reaction was quenched with water. Phosphate buffer (1 M, 10 mL, pH 7.0) was added and the mixture was extracted with diethyl ether. Usual work-up of the organic yielded a crude product that was purified by silica gel chromatography with 1:1 ethyl ether: hexane to give a white solid (42 % yield). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.14-1.38 (m, 14H), 1.62 (m, 2H), 1.77 (m, 2H) 2.35 (s, 3H), 2.61 (t, J7.7, 2H), 3.32 (t, J6.8, 2H), 7.05 (m, 2H), 8.17 (m, 2H), 8.48 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 156.0, 156.0, 152.9, 148.9, 148.8, 148.1, 124.6, 123.9, 122.0, 121.3, 35.5, 34.0, 32.8, 30.4, 29.4, 29.4, 29.3, 29.2, 28.7, 28.1, 21.2.

Preparation of 1-ethyl-1'-[4-(4'-methyl-2,2'-bipyridin-4-yl)butyl]-4,4'-bipyridinium dibromide (**Bipy3-A**)

A mixture of **Bipy3** (702 mg, 1.05 mmol) and **A** bromide (293 mg, 1.10 mmol) in CH₃CN (10 mL) was heated at 90°C for 48 h in a sealed tube. The resulting yellow precipitate was filtered off and washed with hot acetonitrile and diethyl ether, yielding 394 mg (61%) of the product. ¹H NMR (300 MHz, DMSO) δ (ppm): 1.17–1.35 (m, 14H), 1.60 (m, 5H), 1.95 (m, 2H), 2.40 (s, 3H), 2.67 (t, *J* 7.7, 2H), 4.70 (m, 4H), 7.26 (m, 2H), 8.20 (m, 2H), 8.52 (m, 2H), 8.78 (m, 4H), 9.40 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 155.2, 155.1, 152.3, 149.0, 148.9, 148.5, 148.4, 147.9, 145.7, 145.6, 126.6, 126.5, 124.8, 124.1, 121.2, 120.4, 60.8, 56.5, 34.5, 30.7, 29.8, 28.8, 28.7, 28.5, 28.3, 25.4, 20.7, 16.27.

Preparation of Dyad 3

A mixture of **Bipy3-A** (280 mg, 0.418 mmol) and *cis*-bis(2,2'-bipyridine)dichlororuthenium (264 mg, 0.544 mmol) in ethanol : water (7 : 3, 19 mL) was heated at 110°C for 24 h protected from ambient light. The mixture was concentrated under vacuum to yield 590 mg of a dark solid that was used to prepare **3** without further purification. ¹H NMR (300 MHz, DMSO) δ (ppm): 1.20–1.34 (m, 14H), 1.59 (t, 3H), 1.64 (m, 2H), 1.96 (m, 2H), 2.51 (s, 3H), 2.75 (m, 2H), 4.79 (m, 4H), 7.37 (m, 2H), 7.53 (m, 6H), 7.71 (m, 4H), 8.15 (m, 4H), 8.86 (m, 10H), 9.48 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 16.32, 20.64, 25.47, 28.46, 28.79, 28.84, 28.94, 29.51, 30.83, 34.43, 55.97, 60.71, 124.40, 124.50, 125.28, 126.60, 127.81, 128.56, 137.74, 137.69, 145.64, 145.79, 148.50, 149.76, 150.22, 150.40, 151.05, 151.12, 151.17, 154.03, 156.02, 156.17, 156.58, 156.62.

Preparation of 4,4' -bis(4-bromobutyl)-2,2' -bipyridine (*Bipy4*)

Butyllithium (1.59 M in hexane, 7.5 mL, 11.94 mmol) was added to a solution of diisopropylamine (1.5 mL, 11.94 mmol) in THF (23 mL) at -78° C. The mixture was stirred for 45 min and

then added to a solution of 4,4'-dimethyl-2,2'-bipyridine (1 g, 5.43 mmol) in THF (38 mL) at -78° C. After 1 h at 78°C, the resulting brown–red solution was treated with dibromopropane (2.2 mL, 21.68 mmol) and, after stirring for 1 h, a pale green colour developed. The mixture was allowed to reach room temperature for 3 h and the reaction was quenched with water. Phosphate buffer (1 M, 10 mL, pH 7.0) was added and the mixture was extracted with diethyl ether. Usual work-up of the organic layer yielded a crude product that was purified by silica-gel chromatography with 1 : 1 ethyl ether : hexane to give a white solid (1.27 g, 55%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.90 (m, 8H), 2.73 (t, *J* 7.3, 4H), 3.42 (t, *J* 6.4, 4H), 7.12 (d, *J* 4.9, 2H), 8.24 (m, 2H), 8.56 (d, *J* 4.9, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 28.50, 31.95, 33.11, 34.26, 120.92, 121.77, 123.55, 124.48, 147.85, 148.68, 148.87, 151.487, 155.69, 156.02.

Preparation of 1,1'-[2,2'-bipyridine-4,4'-diylbis(butane-4,1-diyl)]bis(1'-ethyl-4,4'-bipyridinium) tetrabromide (*Bipy4-A*)

A mixture of **Bipy4** (1.27 g, 2.98 mmol) and **A** bromide (1.66 g, 6.27 mmol) in CH₃CN (38 mL) was heated at 90°C for 48 h in a sealed tube. The resulting yellow precipitate was filtered off and washed with hot acetonitrile and diethyl ether, yielding 300 mg (62 %) of the product. ¹H NMR (300 MHz, DMSO) δ (ppm): 1.60 (t, *J* 7.4, 6H), 1.72 (m, 4H), 2.06 (m, 4H), 2.77 (t, *J* 7.5, 4H), 4.76 (m, 8H), 7.32 (d, *J* 4.8, 2H), 8.24 (s, 2H), 8.55 (d, *J* 4.8 Hz; 2H), 8.81 (m, 8H), 9.43 (m, 8H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 16.27, 26.21, 30.27, 33.80, 56.52, 60.58, 120.54, 124.27, 126.52, 126.61, 145.59, 145.75, 148.40, 148.47, 149.00, 151.46, 155.00.

Preparation of Dyad 4

A mixture of **Bipy4-A** (489 mg, 0.511 mmol) and *cis*-bis (2,2'-bipyridine)dichlororuthenium (322 mg, 0.664 mmol) in ethanol: water (7:3, 24 mL) was heated at 110°C for 24 h, protected from ambient light. The mixture was concentrated under vacuum to yield quantitatively a dark solid that was used to prepare **4** without further purification. ¹H NMR (300 MHz, DMSO) δ (ppm): 1.60 (t, *J* 7.2, 6H), 1.81 (m, 4H), 2.08 (m, 4H), 2.90 (t, *J* 6.8, 4), 4.77 (m, 4H), 4.89 (m, 4H), 7.43 (d, *J* 5.9, 2H), 7.50–7.60 (m, 6H), 7.69–7.75 (m, 6H), 8.12–8.19 (m, 4H), 8.90 (m, 12H), 9.49 (m, 4H), 9.65 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 16.42, 25.54, 30.27, 33.32, 56.34, 60.07, 124.58, 126.62, 127.88, 128.03, 137.78, 145.66, 145.90, 148.39, 150.33, 151.09, 151.16, 153.20, 156.29, 156.51, 156.61.

General Procedure of Intercalation of Dyads inside γ -ZrP

 γ -ZrP (400 mg) was added to a 1 : 1 water : acetone solution (40 mL) and the suspension was stirred at 80°C for 35 min to attain complete exfoliation of the layers. The dyad to be intercalated was dissolved in a 1 : 1 water : acetone solution (33.4 mL), and added to the γ -ZrP suspension. The mixture was maintained at 80°C for 72 h, and the solid was centrifuged at 5–10g for 15 min at room temperature, washed thrice for 20 min with distilled water and centrifuged under the same conditions again. The washing–centrifugation procedures were repeated twice. The resulting orange solid was dried in the oven at 100°C for 24 h and conditioned for at least 3 h in a desiccator that contained a saturated solution of BaCl₂.

Diffuse Reflectance UV-Vis Spectra

Optical spectra in the 200–800 nm region were recorded on a Cary 5G spectrophotometer for the powdered samples, using the

diffuse reflectance mode and an integrated sphere. BaSO₄ was used as the reference. The remittance (*R*) from the instrument was recorded and the spectra plotted as the Kubelka–Munk function ($F(R) = (1-R)^2/2R$). The band gap of γ -ZrP was estimated from the onset of the absorption band (330 nm) by applying the equation: E (eV) $\approx 1240/\lambda$ (nm).

Solar Cell Preparation

A series of photo-electrochemical cells were prepared by depositing a micrometric layer of the corresponding y-ZrP material as a paste onto a conducting transparent electrode FTO, using the doctor blade technique. The surface of the FTO electrode onto which the film is deposited is defined by means of two parallel strips of adhesive Scotch tapes. The final area obtained was $1 \times 1 \text{ cm}^2$. The film was dried at 150°C for 15 min to remove the terpineol from the paste. The paste was obtained by stirring 100 mg γ -ZrP material in a 3 : 1 mixture of acetone : α -terpineol (4 mL). The electrode-containing material was immersed in an ethanolic basic solution of N535 for 12 h. The platinum counter electrode was produced by thermal decomposition of H₂PtCl₆ in isopropanol solution. The ZrP electrode was assembled with the platinum-based transparent conducting glass using a double sided adhesive polymer film (Surlyn, DuPont) that acts as a separator and sealing element. The two electrodes were held together by hot melting the Surlyn seal at 100°C while applying pressure. The electrolyte (0.5 M lithium iodide and 0.05 M iodine in methoxypropionitrile) was introduced into the cell through the two holes that were drilled in the counter electrode.

Photovoltaic Response Measurements

To determine the J-V plots, the cell was connected to a source meter (Keithley 2601) using metallic clamps covered with gold. The voltage scan was controlled using ReRa Tracer software. The data were automatically transferred to a PC that controlled the experiment and, at the same time, provided datastorage capability to the system. The solar simulator (Sun 2000, ABET Technologies) was adapted to the AM 1.5G filter and the nominal power for the measurements was $100 \,\mathrm{mW \, cm^{-2}}$. The same cells were used to record the incident photon-to-electron conversion efficiency (IPCE) spectra. For the IPCE measurements the sample was excited with a 150-W xenon lamp through a Czerny-Turner monochromator. The current output at short circuit was measured by a potentiostat (AMEL), which transferred the data through the A/D converter to the PC controlling the monochromator apparatus. IPCE curves were calculated using a Newport (818-UV-L) calibrated photodiode.

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References

- D. M. Poojary, B. Zhang, Y. Dong, G. Peng, A. Clearfield, J. Phys. Chem. 1994, 98, 13616. doi:10.1021/J100102A029
- [2] E. Brunet, "How Laminar Zirconium Phosphates Can Make Organic Molecules Display New Behavior and Properties at the Supramolecular

Level in the Solid State", Chapter 9 (**2012**), 279–316; in Metal Phosphonate Chemistry, From Synthesis to Applications, (Abraham Clearfield, Kostantinos D. Demadis, Eds.) RSC Publishing.

- [3] (a) E. Brunet, M. Huelva, R. Vázquez, O. Juanes, J. C. Rodríguez-Ubis, *Chem. –Eur. J.* 1996, 2, 1578. doi:10.1002/CHEM.19960021217
 - Figure 2, path **B** (b) E. Brunet, H. M. H. Alhendawi, O. Juanes, J. C. Rodríguez-Ubis, *J. Mex. Chem. Soc.* **2009**, *53*, 155.

(c) G. Alberti, E. Brunet, C. Dionigi, O. Juanes, M. J. de la Mata, J. C. Rodríguez-Ubis, R. Vivani, *Angew. Chem. Int. Ed.* **1999**, *38*, 3351. doi:10.1002/(SICI)1521-3773(19991115)38:22<3351::AID-ANIE3351>3.0.CO;2-V

(d) E. Brunet, O. Juanes, M. J. de la Mata, J. C. Rodríguez-Ubis, *Angew. Chem., Int. Ed.* **2004**, *43*, 619.

Figure 2, path C (e) E. Brunet, M. J. de la Mata, H. M. H. Alhendawi, C. Cerro, M. Alonso, O. Juanes, J. C. Rodríguez-Ubis, *Chem. Mater.* **2005**, *17*, 1424. doi:10.1021/CM048754Q

(f) E. Brunet, M. J. de la Mata, O. Juanes, H. M. H. Alhendawi, C. Cerro, J. C. Rodríguez-Ubis, *Tetrahedron: Asymmetry* **2006**, *17*, 347. doi:10.1016/J.TETASY.2006.01.014

Figure 2, path **D** (g) R. Fernández-Ruiz, J. C. Rodríguez-Ubis, A. Salvador, E. Brunet, O. Juanes, *J. Anal. At. Spectrom.* **2010**, *25*, 1882. doi:10.1039/C0JA00043D

(h) E. Brunet, O. Juanes, L. Jiménez, J. C. Rodríguez-Ubis, *Tetrahedron Lett.* **2009**, *50*, 5361. doi:10.1016/J.TETLET.2009.07.027

 (i) E. Brunet, H. M. H. Alhendawi, O. Juanes, L. Jiménez,
 J. C. Rodríguez-Ubis, *J. Mater. Chem.* 2009, 19, 2494. doi:10.1039/ B817317F

(j) E. Brunet, M. J. de la Mata, O. Juanes, J. C. Rodríguez-Ubis, *Chem. Mater.* **2004**, *16*, 1517. doi:10.1021/CM0353106

Figure 2, path **E** (k) E. Brunet, M. Alonso, C. Cerro, O. Juanes, J. C. Rodríguez-Ubis, A. E. Kaifer, *Adv. Funct. Mater.* **2007**, *17*, 1603. doi:10.1002/ADFM.200700048

(I) E. Brunet, M. Alonso, M. J. de la Mata, S. Fernández, O. Juanes,
 O. Chavanes, J. C. Rodríguez-Ubis, *Chem. Mater.* 2003, 15, 1232.
 doi:10.1021/CM025778T

Figure 2, path **F** (m) E. Brunet, H. M. H. Alhendawi, C. Cerro, M. J. de la Mata, O. Juanes, J. C. Rodríguez-Ubis, *Microporous Mesoporous Mater.* **2011**, *138*, 75. doi:10.1016/J.MICROMESO.2010.09.027

(n) E. Brunet, H. M. H. Alhendawi, C. Cerro, M. J. de la Mata, O. Juanes, J. C. Rodríguez-Ubis, *Chem. Eng. J.* **2010**, *158*, 333. doi:10.1016/J.CEJ. 2010.01.040

(o) E. Brunet, C. Cerro, O. Juanes, J. C. Rodríguez-Ubis, A. Clearfield, *J. Mater. Sci.* **2008**, *43*, 1155. doi:10.1007/S10853-007-2377-0

(p) E. Brunet, H. M. H. Alhendawi, C. Cerro, M. J. de la Mata, O. Juanes,
 J. C. Rodríguez-Ubis, *Angew. Chem., Int. Ed.* 2006, 45, 6918.
 doi:10.1002/ANIE.200602445

Figure 2, path G: unpublished results. Figure 2, path H (q) H. M. H. Alhendawi, E. Brunet, E. Rodríguez-Payán, O. Juanes, J. C. Rodríguez-Ubis, M. Al-Asqalany, *J. Incl. Phenom. Macrocycl.* **2012**, *73*, 387. doi:10.1007/S10847-011-0076-6

[4] (a) M. R. Hoffmann, S. T. Martin, W. Y. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69. doi:10.1021/CR00033A004
(b) B. O'Regan, M. Gratzel, *Nature* **1991**, *353*, 737. doi:10.1038/ 353737A0
(c) M. Grätzel, *J. Photochem. Photobiol.*, *A* **2003**, *4*, 145. doi:10.1016/

S1389-5567(03)00026-1
 E. Brunet, M. Alonso, M. C. Quintana, P. Atienzar, O. Juanes,

- [5] E. Brunet, M. Alonso, M. C. Quintana, P. Atienzar, O. Juanes, J. C. Rodríguez-Ubis, H. García, *J. Phys. Chem. C* 2008, *112*, 5699. doi:10.1021/JP800026R
- [6] L. Teruel, M. Alonso, M. C. Quintana, A. Salvador, O. Juanes, J. C. Rodriguez-Ubis, E. Brunet, H. García, *Phys. Chem. Chem. Phys.* 2009, 11, 2922. doi:10.1039/B816698F
- [7] P. Atienzar, M. Victoria-Rodríguez, O. Juanes, J. C. Rodríguez-Ubis, E. Brunet, H. García, *EnergyEnviron. Sci.* 2011, 4, 4718.
- [8] (a) B. M. Peef, G. T. Ross, G. J. Meyer, T. J. Meyer, B. W. Erickson, *Int. J. Pept. Prot. Res.* 1991, *38*, 114.
 (b) L. Strekowski, J. L. Mokrosz, F. A. Tanious, R. A. Watson, D. Harden, M. Mokrosz, W. D. Edwards, W. D. Wilson, *J. Med. Chem.* 1988, *31*, 1231. doi:10.1021/JM00401A027

