ACCOUNTS
of chemical research

Iridium Terpyridine Complexes as Functional Assembling Units in Arrays for the Conversion of Light Energy

LUCIA FLAMIGNI,*,† JEAN-PAUL COLLIN,*,‡ AND
JEAN-PIERRE SAUVAGE*,‡

†Istituto ISOF-CNR, Via P. Gobetti 101, 40129 Bologna, Italy, ‡Laboratoire de Chimie Organo-Minérale, UMR 7177 CNRS, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, 67070 Strasbourg, France

## CONSPECTUS

In photosynthesis, sunlight energy is converted into a chemical potential by an electron transfer sequence that is started by an excited state and ultimately yields a long-lived charge-separated state. This process can be reproduced by carefully designed multicomponent artificial arrays of three or more components, and the stored energy can be used to oxidize or reduce molecules in solution, to inject electrons or holes, or to create an electron flow. Therefore, the process is important both for artificial-photosynthesis research and for photovoltaic and optoelectronic applications. Molecular arrays for photoinduced charge separation often use chromophores that resemble the natural ones. However, new synthetic components, including transition metal complexes, have had some success.

This Account discusses the use of bis-terpyridine (tpy) metal complexes as assembling and functional units of such multicomponent arrays. $M(tpy)_2^{n+}$ complexes have the advantage of yielding linear arrays with unambiguous geometry. Originally, $Ru(tpy)_2^{2+}$ and $Os(tpy)_2^{2+}$ were used as photosensitizers in triads containing typical organic donors and acceptors. However, it soon became evident that the relatively low excited state of these complexes could act as an energy drain of the excited state of the photosensitizer and, thus, seriously compete with charge separation.

A new metal complex that preserved the favorable tpy geometry and yet had a higher energy level was needed. We identified $Ir(tpy)_2^{3+}$, which displayed a higher energy level, a more facile reduction that favored charge separation, a longer excited-state lifetime, and strong spectroscopic features that were useful for the identification of intermediates. $Ir(tpy)_2^{3+}$ was used in arrays with electron-donating gold porphyrin and electron-accepting free-base porphyrins. A judicious change of the free-base porphyrin photosensitizer with zinc porphyrin allowed us to shape the photoreactivity and led to charge separation with unity yield and a lifetime on the order of a microsecond.

In a subsequent approach, an $Ir(tpy)_2^{3+}$ derivative was connected to an amine electron donor and a bisimide electron acceptor in an array 5 nm long. In this case, the complex acted as photosensitizer, and long-lived charge separation over the extremities (>100 μs, nearly independent of the presence of oxygen) was achieved. The efficiency of the charge separation was modest, but it was improved later, after a modification aiming at decoupling the donor and photosensitizer components. This study represents an example of how the performances of an artificial photofunctional array can be modeled by a judicious design assisted by a detailed knowledge of the systems.
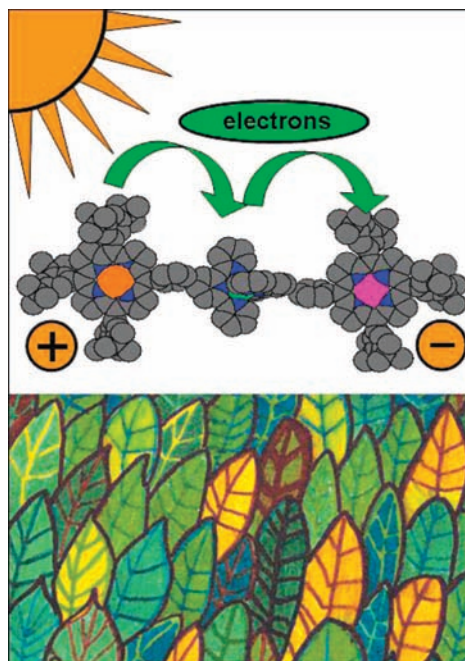
Introduction

The process of moving the electron far from its original position in a molecular array is a way to store energy just like pulling a spring. If we can get light to do the job, this is a way to convert light into a usable form of energy, since the energy accumulated can be used to produce work. It can be used as electrochemical potential to oxidize or reduce molecules in solution, to inject electrons or holes, or to create an electron flow. Photoinduced charge separation, as this phenomenon is called, is one of the central themes of artificial photosynthesis research but has important implications also for photovoltaic and optoelectronic applications. After its elucidation, charge separation occurring in the reaction centers of bacteria has been the model for the design of charge-separation devices. Several ideas borrowed from nature proved to be successful: (i) the rigidity of the structure, which in natural systems is provided by a protein scaffold, was found to be very critical; (ii) multistep electron transfer, consisting in multiple short-distance electron transfers taking the electron a long distance from the hole, has proven to be the winning strategy to achieve long-lived charge-separated (CS) states; (iii) the use of components similar to those found in nature, such as tetrapyrroles, quinones, and carotenes, has characterized the first successful attempts and is still very valuable.[1,2] In the course of the years, however, a large number of efficient CS devices making use of components different from those found in nature has been proposed. Methylviologens, amines, and tetrathiofulvalenes, as well as fullerenes and aromatic bisimide, have found much use as electroactive components by virtue of their remarkable thermodynamic and spectroscopic properties. Transition metal complexes, which had played a key role in the classical photocatalytic studies on water splitting,[3-5] have also been used.[6-8] Here we want to address the results achieved by a relatively new transition metal complex family introduced in our laboratories, namely, Ir^{III} bisterpyridine, as assembling and functional unit in arrays for achieving charge separation.

Design

We will discuss the design of simple triads (three-components arrays) where charge separation over the extremities is produced as a consequence of two electron transfer steps, but the line of reasoning can be extended to higher homologues. In Figure 1, some common cases among the many possible designs are schematically reported.

The components have to be selected on the basis of their redox properties, but their spectroscopic/photophysical traits are important. Care has to be taken to prevent quenching of
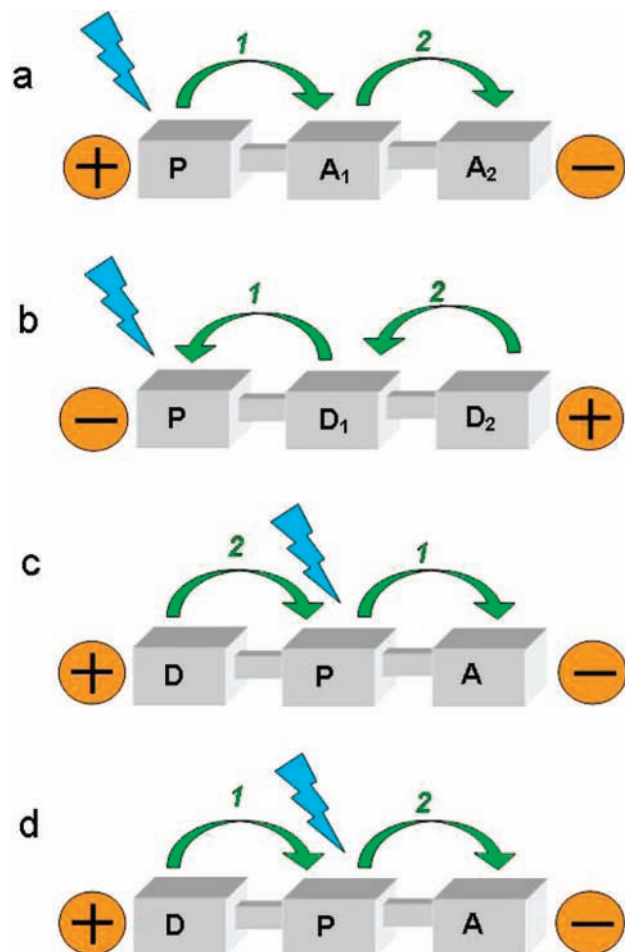
FIGURE 1. The arrows illustrate electron motion and the numbers the chronology of events in typical arrays for charge separation: (a) The excited state of the photosensitizer, *P, transfers an electron to the primary acceptor, A1, and from here an electron is transferred to a secondary acceptor A2, more easily reducible than A1, leading to a CS state with the hole and the electron on the extreme components. (b) *P is reduced by the donor, D1, which is in turn reduced by D2, provided D2 is more easily oxidized than D1. (c) P* can transfer an electron to A and subsequently P$^+$ can accept an electron from D, which can be oxidized more easily than P. An alternative version is case d, where P* can accept an electron from D, and subsequently, the resulting P$^-$ transfers the electron to the unit A, which can be reduced more easily than P.

the excited state of the photosensitizer (P) by energy transfer; therefore both acceptor (A) and donor (D) either should possess higher excited states than P or should display a slow energy transfer reactivity. A desirable quality of the components is that the intermediate radicals and excited states involved have clear and intense spectroscopic features to be unambiguously identified. The component units are connected in Figure 1 by a simple line, but the linker is important, in providing both *electronic communication* and *structural rigidity*. Rigid and linear structures have better chances since rigidity prevents through-space contacts of the extremities and linear-

CHART 1. Three Representative Examples of Molecular Triads Consisting of a Central Ruthenium(II) Complex Acting as Photosensitizer and Peripheral Electron Acceptor and Donor Groups

PTZ$_2$-Ru-DQ

Mn$_2$^{II,II}-Ru-NDI$_2$

M = Ru: DAPA-Ru-MV
M = Os: DAPA-Os-MV
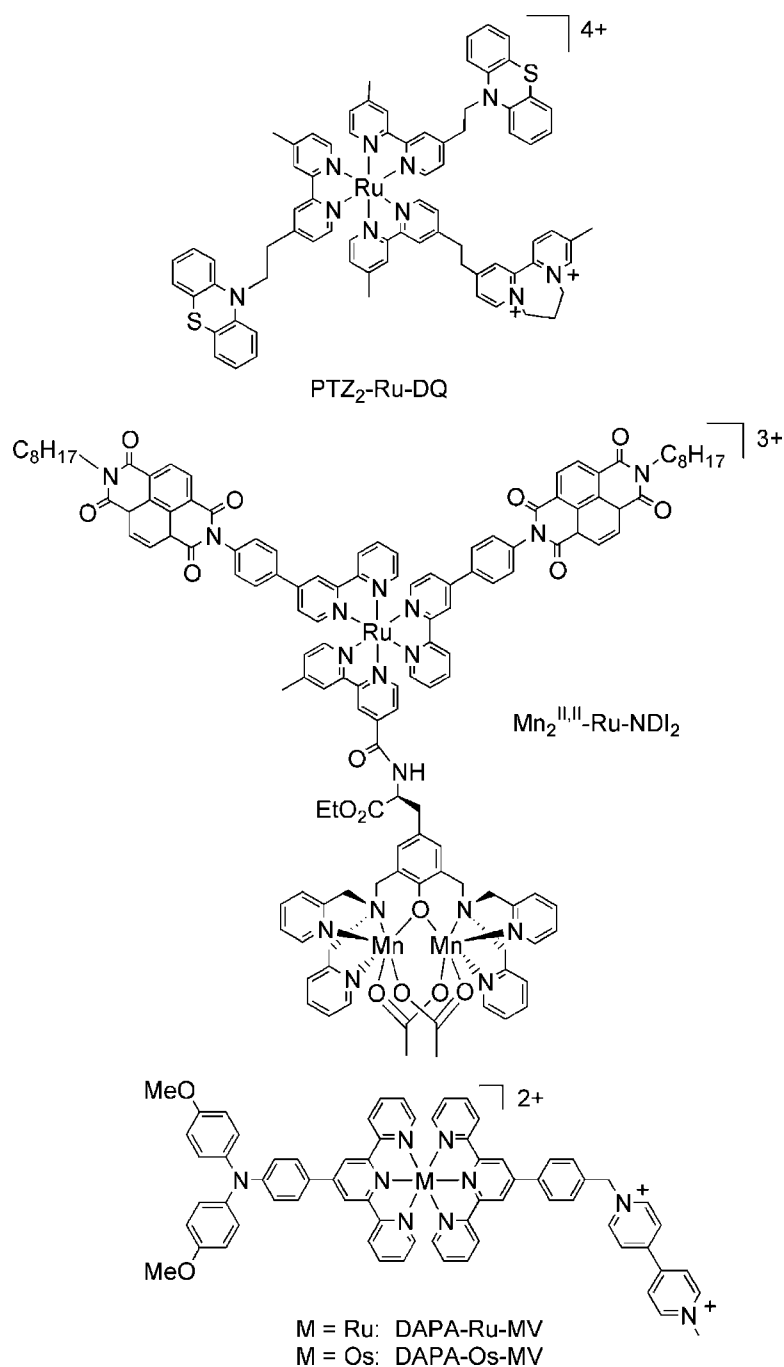
ity provides less ambiguous structure and larger distance between extremities.

Previous Related Systems. Ru(bpy)$_3$$^{2+}$, where bpy is 2,2′-bipyridine, has been used more often than any other metal complex.[7,8] In Chart 1 one of the first systems, PTZ$_2$−Ru−DQ, studied by Meyer, Elliot, and co-workers, and an important recent achievement, Mn$_2$^{II,II}−Ru−NDI, reported by Johansson, Magnuson, and Hammarström, are reported.[9,10]

In the early example, flexible methylene connections link the electron donor phenothiazine (PTZ) and the bridged 2,2′-bipyridinium (DQ) to the ruthenium complex in PTZ$_2$−Ru−DQ. Excitation at the Ru-based chromophore ultimately yields a PTZ$^+$−Ru−DQ$^-$ CS state, which lives for 165 ns at room temperature and for which the stored energy is 1.29 eV. Light absorption at the Ru(bpy)$_3$$^{2+}$ photosensitizing unit in the multicomponent system Mn$_2$^{II,II}−Ru−NDI$_2$, including a manga-
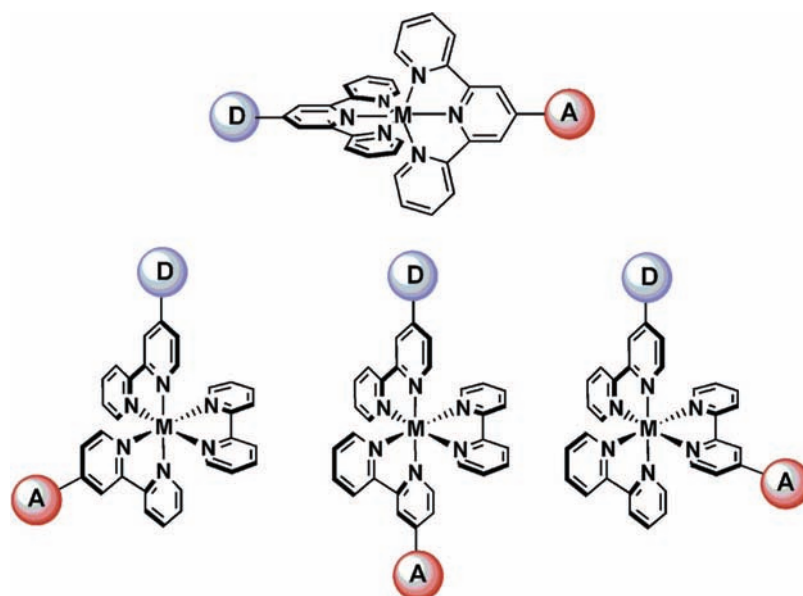
FIGURE 2. The single isomer derived from M(tpy)$_2$$^{n+}$ substitution at the 4′ positions is displayed with some of the isomers derived from M(bpy)$_3$$^{n+}$ upon 4 and 4′ substitutions.

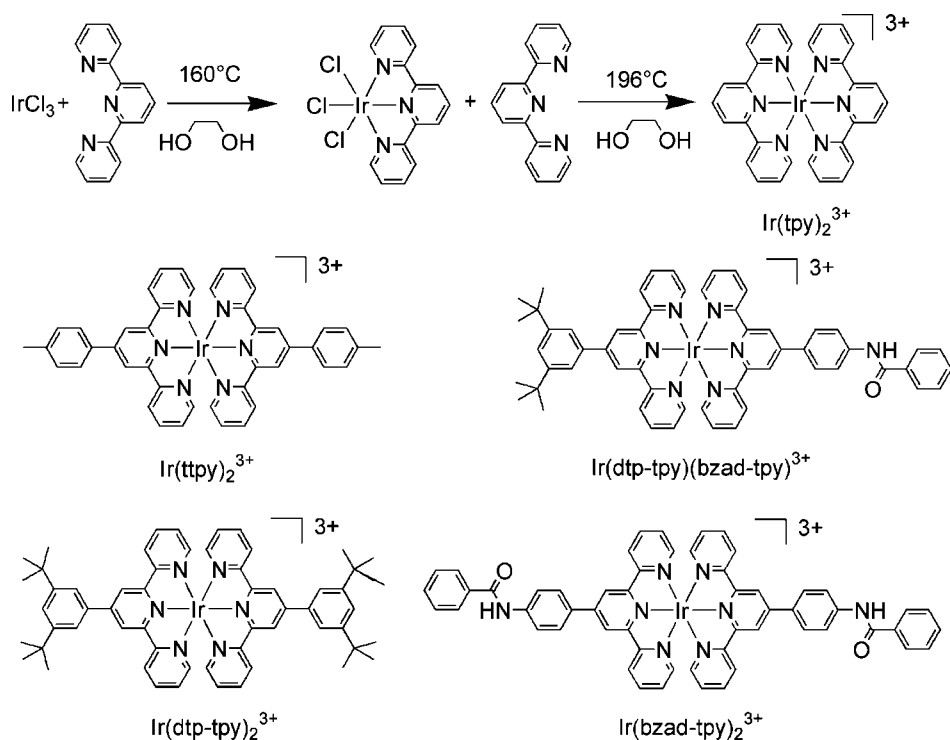**CHART 2.** Triads Combining Porphyrins and a Ruthenium(II) Center

M = 2H : PH$_2$-Ru-PAu
M = Zn : PZn-Ru-PAu

M = 2H : PH$_2$′-Ru-PAu
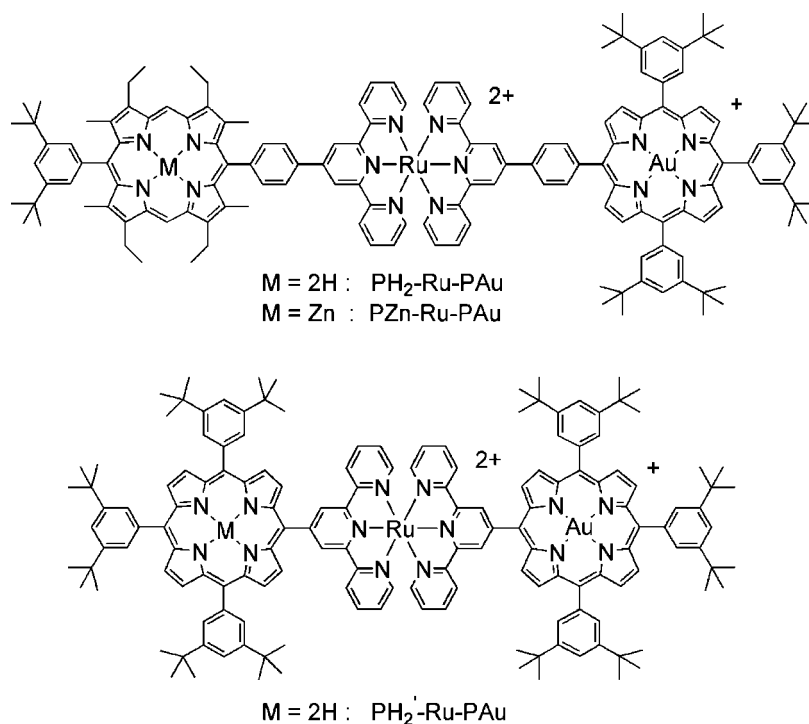
nese dimer moiety (Mn$_2$^{II,II}) and two naphthalenediimide (NDI) units, results in oxidation of the manganese dimer to Mn$_2$^{II,III} and NDI reduction to NDI$^-$, a CS state with an impressive $\tau =$ 600 μs at room temperature and a stored energy of 1.07 eV.

One can notice that the bidentate bpy ligand arrangement does not provide a convenient environment for the construction of linear D−complex−A arrays and is characterized by geometrical and optical isomers upon substitution at the 4 and

4′ positions. (Figure 2). In contrast, the geometry of the Ru(tpy)$_2$$^{2+}$ where tpy is 2,2′:6′,2″-terpyridine is ideal for the construction of linear, rigid arrays with univocally determined structure. Whereas the excited-state energy of Ru(tpy)$_2$$^{2+}$ is only slightly lower than that of Ru(bpy)$_3$$^{2+}$ and the redox properties are similar, the lifetime of the excited state of the former is much shorter (1 ns) than the lifetime of the latter (1 μs). The latter issue, which is very critical for *intermolecular* sensitiza-
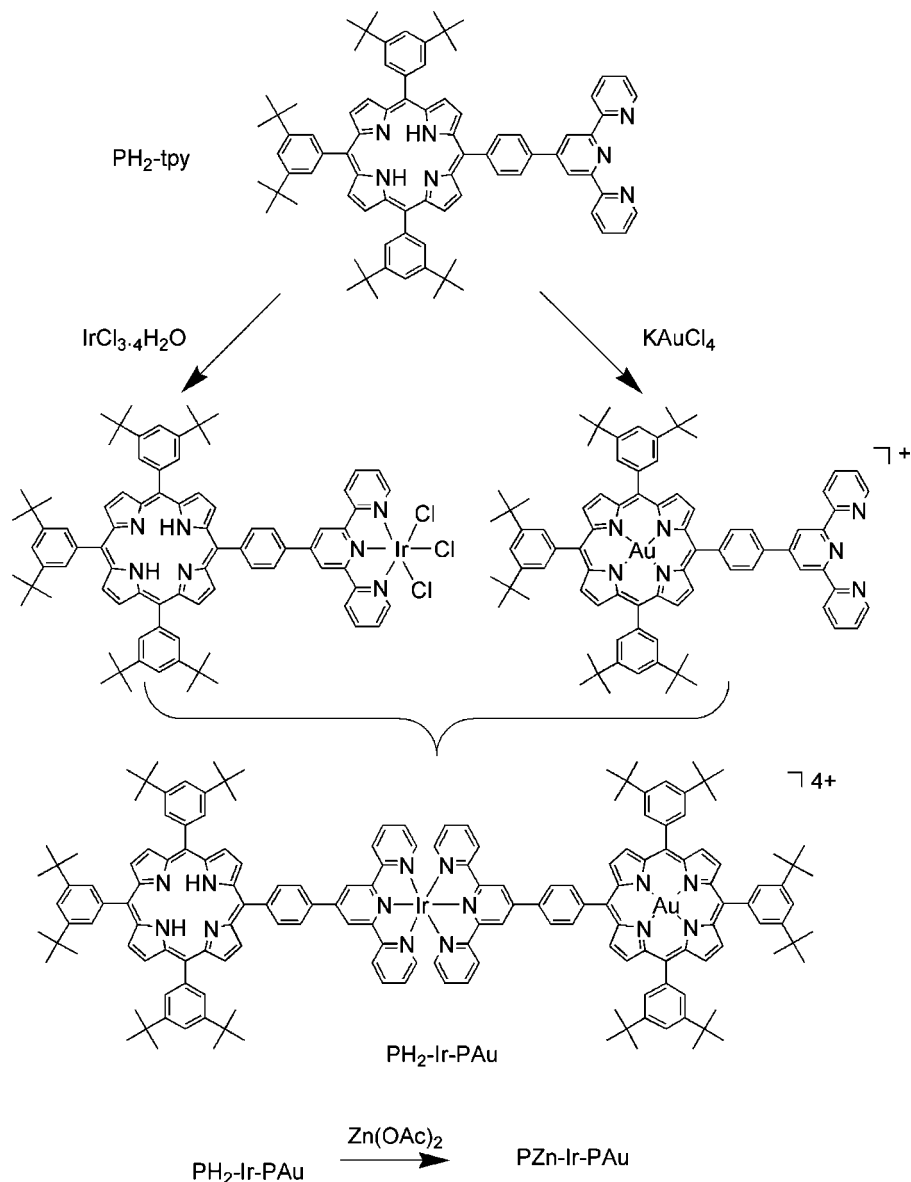
CHART 3. The Stepwise Preparation of Iridium(III) Bis-terpyridine Type Complexes Allowing Symmetrical and Dissymmetrical Complexes To Be Obtained

tion because of the necessary diffusion time of the sensitizer toward the electron acceptor, is less important in *intramolecular* sensitization reactions. Most of the excited-state reactions within an array are, in fact, several orders of magnitude faster than the intrinsic deactivation rate of the excited state. The short sensitizer lifetime is thus unimportant in most cases.

We used terpyridine complexes of Ru^{II} and Os^{II} as assembling and functional components of photoactive triads since the early 1990s. In our first attempts, the photosensitizer $Ru(tpy)_2^{2+}$ (Ru) was connected to a typical organic electron donor such as di-*p*-anisylphenylamine (DAPA) on one side and to the electron acceptor methylviologen (MV) on the other.[11] Excitation in the metal-to-ligand charge transfer (MLCT) band of the metal complex in the DAPA−Ru−MV triad (Chart 1) led to a CS state with opposite charges over the extremities, according to the step sequence reported in Figure 1c. The lifetime at 155 K was 27 ns. The corresponding Os^{II}-based triad did not lead to any long-lived CS state over the extremities.[12] A further development of the project made use of porphyrins as components to increase the light absorption in the visible range. Ru was connected to a porphyrin electron donor, either a Zn^{II} porphyrin (PZn) or a free-base porphyrin (PH$_2$), and to a Au^{III} porphyrin cation electron acceptor (PAu), Chart 2. In the ensuing triad PZn−Ru−PAu (or PH$_2$−Ru−PAu), PZn (or PH$_2$) porphyrin plays the role of photosensitizer, whereas Ru acts as electron relay.

While the first triads making use of etio-type porphyrins as electron donors seemed to be successful in producing CS states with lifetimes of several tens of nanoseconds,[13] replacement with the more robust tetra-aryl porphyrin PH$_2$′ in PH$_2$′−Ru−PAu changed dramatically the reactivity.[14] Tetra-aryl porphyrins are in fact less fragile both at the synthetic stage and under light, but their excited states are slightly lower than that of the corresponding etio-type porphyrin, while their oxidation potentials are slightly higher. This led to a thermodynamically more allowed quenching by energy transfer of the porphyrin excited state rather than a quenching by electron transfer. The energy transfer path from the singlet excited state of porphyrins to the triplet MLCT of Ru is spin-forbidden; however the presence of the heavy Ru ion enhances spin−orbit coupling allowing the occurrence of this step.[14]

From these studies, it clearly emerges that $Ru(tpy)_2^{2+}$ is far from being ideal and that there is the need to identify a different metal complex as component unit. The characteristics of this new metal complex would be *higher excited states* and *easier reduction*, preserving the favorable geometry provided by the terpyridine. The former characteristic would prevent quenching of the sensitizer excited state by energy transfer; the latter would stabilize the CS state formed upon electron transfer from the porphyrin sensitizer to the metal complex unit, increasing the driving force, and hence the efficiency, of the primary charge-separation step. In addition, the complex

CHART 4. Synthesis of the Two Porphyrinic Triads PH$_2$−Ir−PAu and PZn−Ir−PAu

should be chemically stable and kinetically inert to prevent possible scrambling of the ligands bound to the metal and thus destruction of the triad structure.

Ir Terpyridine Type Complexes. Among the available metals, the Ir^{III} trication (a 5d^6 center) seemed to be a good choice. The electronic properties of its polyimine complexes share several features with those of other octahedral complexes of the most common Ru^{II} and Os^{II}.[15] The exploitation of Ir^{III} terpyridine complexes was considered, and a series of Ir(tpy)$_2$$^{3+}$ complexes was synthesized and characterized from the electrochemical, spectroscopic, and photophysical points of view in our laboratories.[16,17]

The iridium(III) reference complexes depicted in Chart 3 have been prepared in a stepwise method. Ir(tpy)$_2$$^{3+}$ had been

reported long ago by DeGraff, Demas, and co-workers,[18] who could prepare this complex under extremely harsh conditions (fusion reaction) in a one-step reaction. Unfortunately, the yield was poor, and the purification procedure was described as "arduous". It thus seemed to be indispensable to develop more efficient and practical experimental procedures for making Ir(tpy)$_2$$^{3+}$ and related complexes. In addition, if we want to make and study dyads or triads of the D−P−A family, the preparation of asymmetric complexes is crucial, which implies stepwise coordination of two distinct tpy derivatives. After many trials under various conditions using the commercially available tpy ligand, the conditions were gradually improved so as to afford a reasonably high-yielding procedure. The key characteristic of the synthesis is the use of different condi-

CHART 5. Preparation of the Dyads PH$_2$−Ir and PAu−Ir
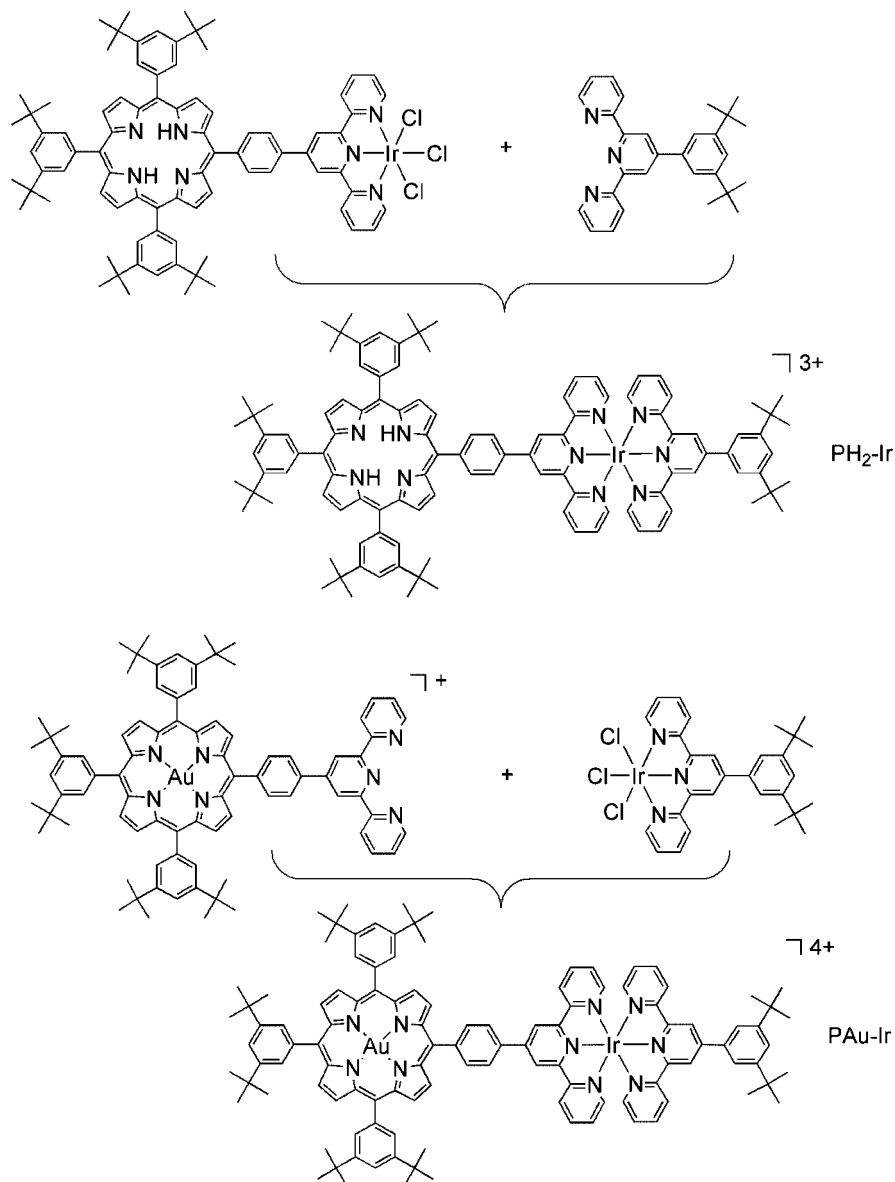
tions for the first and the second tpy coordination reaction, with a significant increase of the reaction temperature from step 1 to step 2 (160 to 196 °C). The choice of ethylene glycol as solvent was also determining: this high-boiling point solvent can also play the role of a mild reductant, thus preventing detrimental oxidation of the ligands used. In fact, the solvent itself could be oxidized instead of the chemically sensitive functions borne by some of the ligands. As one would expect, coordination of the first terpyridine is easier than the introduction of the second one, the latter requiring dechlorination of the Ir(tpy)Cl$_3$ precursor. Depending on the nature of the terpyridine ligand, the first step can be performed either under harsh conditions (refluxing ethylene glycol) or in refluxing ethanol.

The main characteristics of Ir(tpy)$_2$$^{3+}$ in comparison with the Ru(tpy)$_2$$^{2+}$ compound can be summarized as follows. The first ligand reduction, occurring at ca. −0.8 V vs SCE, is easier than that for Ru(tpy)$_2$$^{3+}$ the ligand of which can be reduced at around −1.3 V vs SCE. This is a consequence of the larger ionic charge in the Ir(III) center. Due to the same reason, the metal-centered oxidation step is much more difficult in Ir(tpy)$_3$$^{3+}$, exceeding the +2.4 vs SCE potential used for the experiments, than in Ru(tpy)$_2$$^{3+}$ where the oxidation potential is +1.29 V. The spectroscopic absorption features of the Ir^{III} derivatives appear at higher energy than the Ru^{II} counterpart; the typical ^{1}MLCT band around 490 nm of Ru(tpy)$_2$$^{3+}$ (ε on the order of 10^4 M^{-1} cm^{-1}) is absent, and the absorption onset is below 450 nm in the iridium derivatives, Figure 3.

TABLE 1. Spectroscopic, Photophysical, and Electrochemical Parameters of Complexes in Air Equilibrated CH_3CN

	absorption		emission			electrochemistry	
	λ_{abs} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{em} (nm)	ϕ_{fl}	τ (μs)	oxidation, $Ir^{IV/III}$ (V vs SCE)	reduction, $L^{0/-1}$ (V vs SCE)
$Ir(tpy)_2^{3+}$	352	5.8	458	0.025	1.0	>2.4	−0.77
$Ir(ttpy)_2^{3+}$	373	29.0	506	0.029	2.4	>2.4	−0.81[a]
$Ir(dtp\text{-}tpy)_2^{3+}$	372	23.8	506	0.022	1.6	>2.4	−0.74
$Ir(bzad\text{-}tpy)_2^{3+}$	410	46.0	566	0.0027	0.58	2.4	−0.76

[a] In dichloromethane.
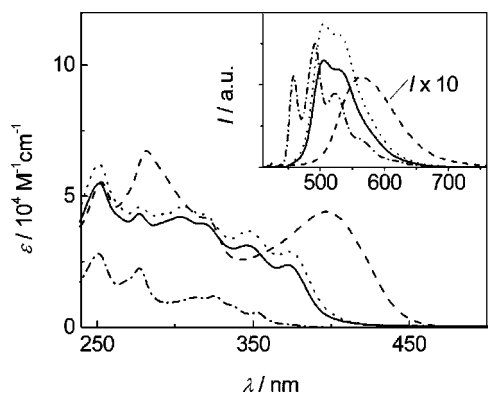
FIGURE 3. Absorption and luminescence (inset) spectra of $Ir(tpy)_2^{3+}$ (−·−), $Ir(ttpy)_2^{3+}$ (···), $Ir(dtp\text{-}tpy)_2^{3+}$ (−), and $Ir(bzad\text{-}tpy)_2^{3+}$ (−−−) in CH_3CN, room temperature.
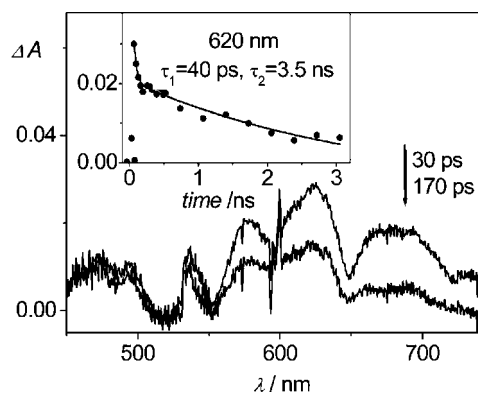
FIGURE 4. Transient absorption in CH_3CN solutions of $PH_2-Ir-PAu$. In the inset, the time profile of the decay and the exponential fittings are displayed.

The wavelength maximum for a few representative cases is reported in Table 1 with other parameters. A few remarks can be made on the energy of the various transitions: (i) metal-centered (MC) bands are expected at high energy; (ii) spin-allowed transitions to ^{1}MLCT, due to the difficulty to oxidize the Ir^{III} metal center, are also expected at high energy; (iii) spin-forbidden ^{3}MLCT absorption bands, made possible by the heavy metal effect, could contribute to the absorption bands at low energy. Therefore, in this type of complex, ligand-centered (LC) excited states can come into play as relatively low-energy transitions. Luminescence, as noticed for all heavy metal complexes, occurs from a formal triplet state because of the high spin–orbit coupling and is reported in Figure 3, inset.

Identification of the emitting state nature can be assisted by the examination of some luminescence parameters. In particular, (i) ^{3}MLCT emissions yield broad luminescence profiles, while spectra for ^{3}LC emissions are generally narrower and well-resolved, and (ii) ^{3}MLCT as well as other charge transfer (CT) excited states displays a hypsochromic shift of the emission peak in polar solvents on passing from ambient temperature to 77 K in a frozen medium.

Along the series of Table 1, the lowest-lying excited level moves to lower energy as the ligand size gets larger. The emission changes from an essentially ^{3}LC character in $Ir(tpy)_2^{3+}$, to a predominant ^{3}LC with some ^{3}MLCT contamination for $Ir(ttpy)_2^{3+}$ and $Ir(dtp\text{-}tpy)_2^{3+}$, whereas for $Ir(bzad\text{-}tpy)_2^{3+}$ an inversion of the nature of the emitting state can be noticed passing from room temperature to 77 K in a glass. The emission has CT character at room temperature, presumably of intraligand charge transfer (^{3}ILCT) nature, but it turns to ^{3}LC in the glass, as the structured emission profile indicates. In this case, the solvent solidification prevents reorientation about the molecular dipole, and the CT state is strongly destabilized.

In conclusion, the examined series of $Ir(tpy)_2^{3+}$ can satisfy the requirements for the sought metal complex since it exhibits a convenient geometry, high energy levels, and lower reduction potential. One can notice more valuable characteristics of the $Ir(tpy)_2^{3+}$ excited state: (i) a lifetime in the microsecond range with a 3 orders of magnitude increase with respect to $Ru(tpy)_2^{2+}$; (ii) enhanced luminescence quantum yield and intense absorption features of the triplet excited state in the NIR region, both convenient for spectroscopic detection. Another special feature of $Ir(tpy)_2^{3+}$ is the strong electron-accepting character of its excited state at odds with its Ru(II) analog.

Porphyrinic Arrays

The identification of a new assembling and photo- or electro-active metal complex stimulated the design and synthesis of arrays with improved performances. The first idea was that of using the assembling Ir terpyridine derivative, because of the facile reduction, as primary electron acceptor (electron relay)
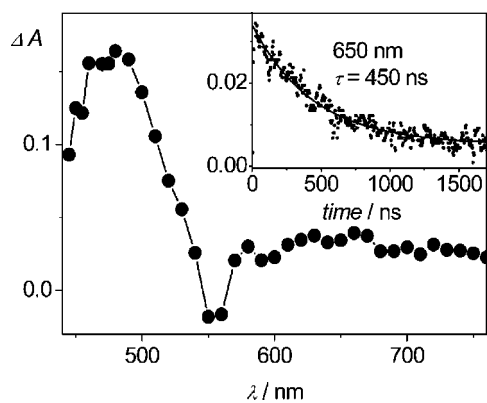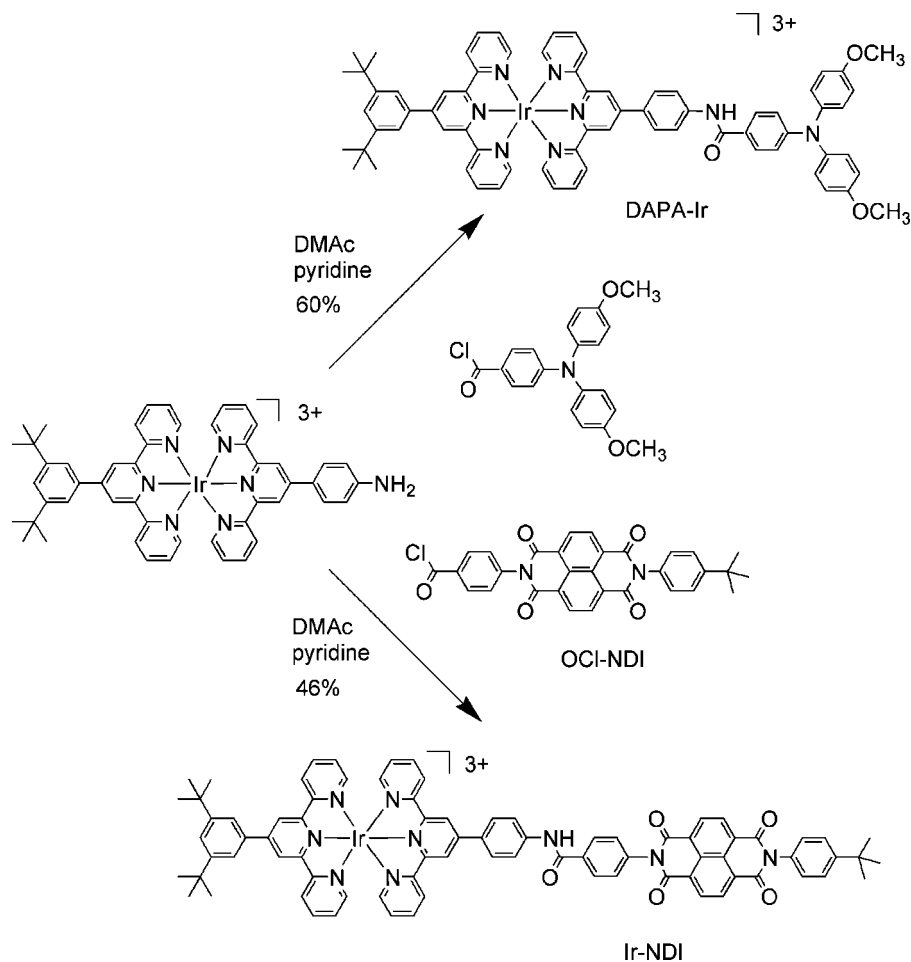
SCHEME 1. Energy Levels and Photoinduced Processes in $PH_2-Ir-PAu$ in Acetonitrile and $PZn-Ir-PAu$ in Toluene

a

b
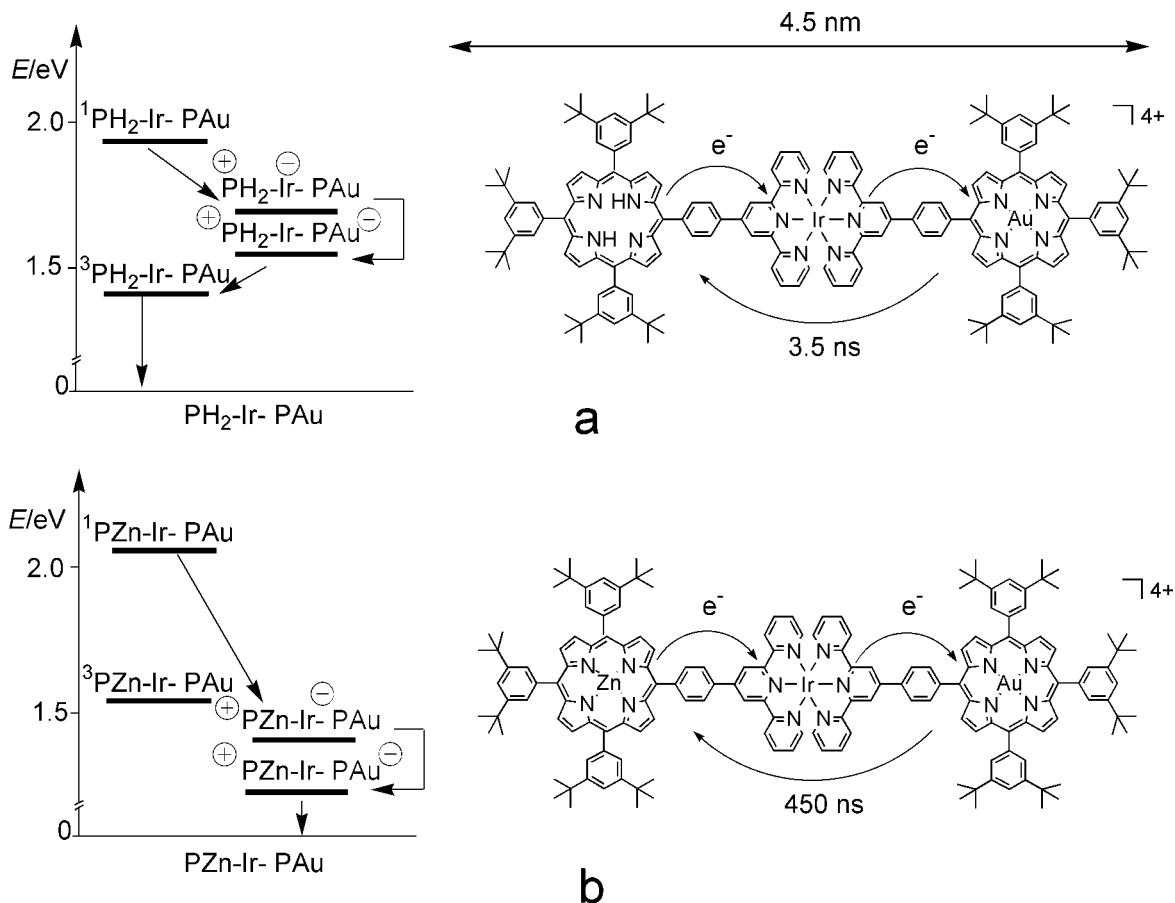
as described in Figure 1a. Borrowing from the biomimetic approach to photosynthesis, we used Zn^{II} porphyrin or free-base porphyrin as photosensitizer, a choice justified by the high extinction coefficients in the visible region of the spectrum, the facile oxidation, and the well-known excited-state properties of these chromophores. The selected secondary acceptor was a porphyrin on which the groups had much experience, a cationic Au^{III} porphyrin characterized by a reduc-

FIGURE 5. Transient absorption in toluene solutions of $PZn-Ir-PAu$ at the end of the pulse. In the inset, the time profile of the decay and the exponential fitting are displayed.

tion potential lower than that of the $Ir(tpy)_2^{3+}$ unit, as required by the design.

In the synthetic strategy used to prepare the various dyads and triads, the key compound is the unsymmetrical porphyrin PH_2-tpy (Chart 4). It illustrates the strong point of the modular approach employed: once the ligand PH_2-tpy is available in sufficient quantities, the dyads PH_2-Ir, $PAu-Ir$, and $PZn-Ir$ and triads $PH_2-Ir-PAu$ and $PZn-Ir-PAu$ are obtained by playing in the right order with the coordination chemistry of zinc(II), iridium(III), and gold(III) (Charts 4 and 5). The unsymmetrical porphyrin PH_2-tpy bearing one tpy substituent was prepared following a Suzuki coupling procedure between a porphyrin bearing a boronic ester and 4'-bromo-2,2':6',2''-terpyridine (Br-tpy). The redox characteristics of the dyads and triads were examined by cyclic voltammetry in CH_3CN and CH_2Cl_2. The redox potentials of the individual components are almost identical in the dyads, triads and reference compounds, that is, ca. -0.78 V for Ir reduction, ca. 0.95 and 0.62 V for the first oxidation of PH_2 and PZn, respectively, and ca. -0.6 V for reduction of PAu (in CH_3CN vs SCE). As a consequence, only weak interactions are inferred among the various com-

CHART 6. Synthesis of Dyads DAPA–Ir and Ir–NDI

SCHEME 2. Energy Levels and Photoinduced Processes in DAPA–Ir–NDI in Acetonitrile
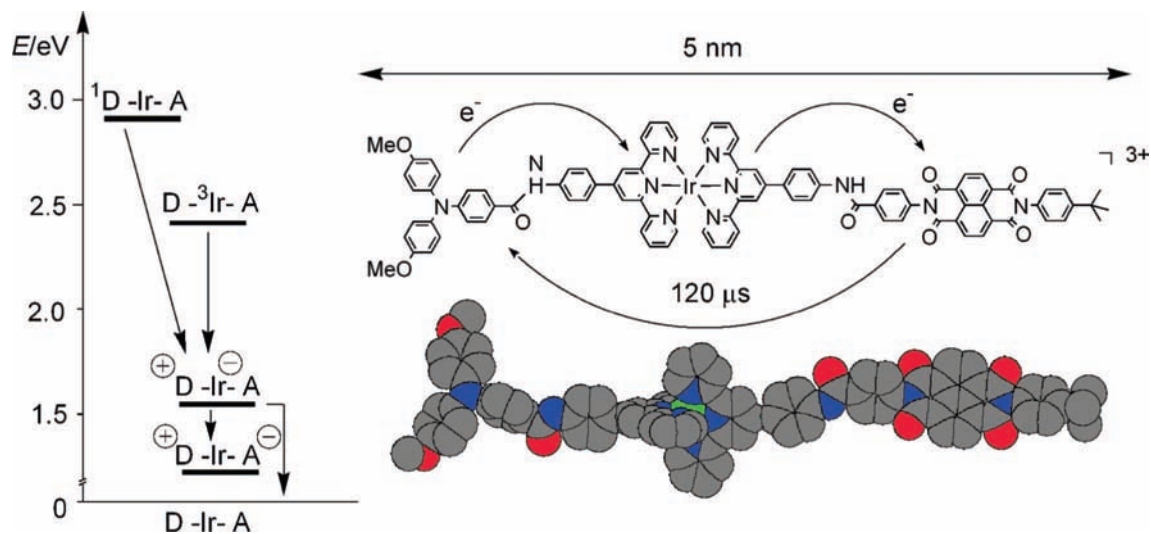
ponents, and a localized description of the individual subunits could be used to predict the properties in the arrays.

The behavior of the free-base series was studied in acetonitrile starting from the examination of the component dyads:

whereas excitation of PAu–Ir in the PAu unit yields no change in the overall reactivity of the components, excitation of the porphyrin units in PH$_2$–Ir led to quenching of the porphyrin luminescence to a lifetime of 30 ps, compared with an 8.3 ns
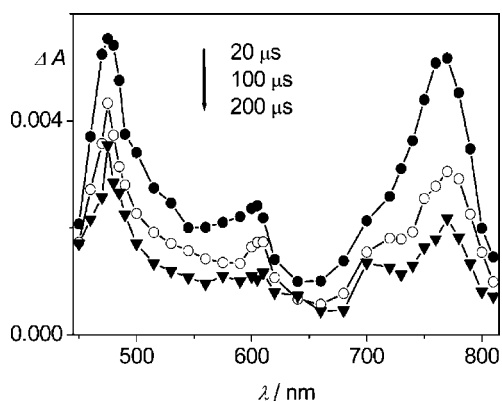
FIGURE 6. Transient absorbance of the CS state of DAPA−Ir−NDI in acetonitrile.

lifetime of PH$_2$. The quenching was assigned to electron transfer from the porphyrin excited state (1.91 eV) to the CS state PH$_2^+$−Ir$^-$, whose energy level could be estimated from electrochemical parameters ca. 0.2 eV lower.

The assignment to electron transfer was confirmed both by the fact that freezing of solvent suppressed quenching and by the detection of the porphyrin cation band (600−700 nm range) decaying with a lifetime of 75 ps. In the triad PH$_2$−Ir−PAu, excitation of the free-base porphyrin sensitizer led to an identical quenching of PH$_2$ luminescence but resulted in the formation of a CS state decaying faster (40 ps) than that in the dyad.[19] This decrease in lifetime is indicative of the presence in the triad of a further step depopulating the state, for which an efficiency of ca. 50% can be calculated. In fact, the spectrum evolved into a longer lived component with a similar spectrum, assigned to the fully charge-separated state PH$_2^+$−Ir−PAu$^-$ in which an energy of ca. 1.5 eV was stored. Contrary to the expectations, the lifetime of the ultimate CS state was disappointingly low, 3.5 ns (Figure 4). This was caused by recombination of the CS state to a closely lying triplet state localized on PH$_2$, as the quantitative determination of the triplet yield could confirm (Scheme 1a).[20]

Replacement of PH$_2$ with PZn, characterized by a lower oxidation potential and by a higher triplet excited-state energy level, changes the ordering of the states in the triad PZn−Ir−PAu, Scheme 1b. For solubility and stability reasons, the experiments were conducted in toluene or dichloromethane. Excitation of the zinc porphyrin sensitizer in the dyad PZn−Ir in dichloromethane led to a very efficient quenching of the porphyrin luminescence, $\tau \leq 20$ ps compared with a lifetime of 1.8 ns for PZn, and the same occurred in the triad. A CS state could be identified by its transient absorption spectra displaying the typical zinc porphyrin cation band ($\lambda_{max} = 670$ nm), but the lifetime of the CS state was

the same, ca. 110 ps, in the dyad PZn−Ir and in the triad PZn−Ir−PAu. This indicates that in the triad, recombination to the ground state occurred essentially from the intermediate CS state PZn$^+$−Ir$^-$−PAu, and no further electron transfer to form the CS state PZn$^+$−Ir−PAu$^-$ occurs in dichloromethane. In contrast, in toluene, the spectrum of the charge-separated state, appearing immediately after the laser pulse, displayed a remarkably long lifetime, 450 ns in air-purged solution (Figure 5). This CS state was formed with 100% yield and could store an energy of ca. 1.3 eV.[20]
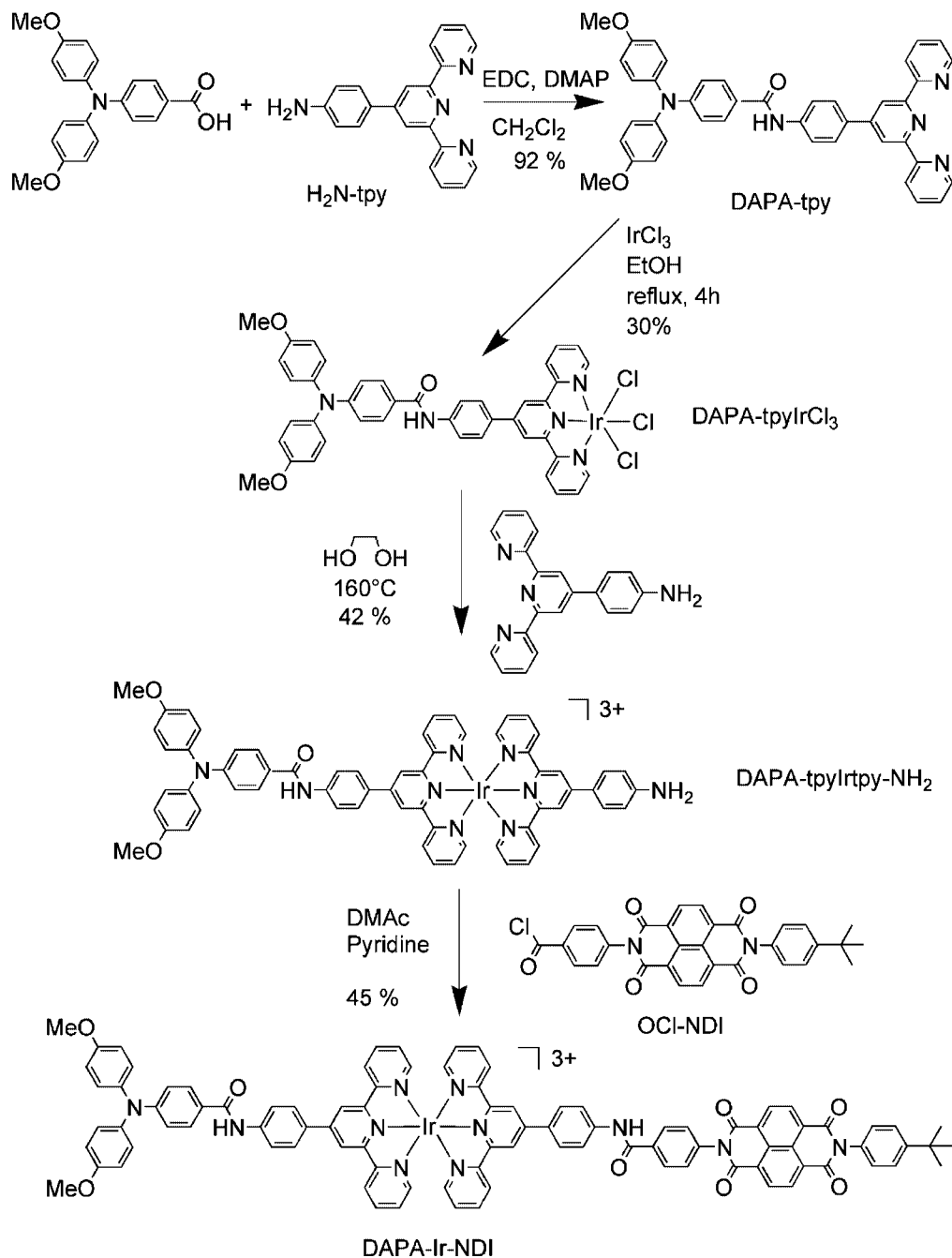
Quite remarkably this system is more efficient as a CS device in low-polarity than in high-polarity solvent, which contrasts with most of the reports on the topic. It should however be remembered that the array PZn−Ir−PAu is ionic, PAu being a monocation, so both ground state and CS state have a positively charged extremity. Under these conditions, the well-known stabilization by polar solvents of CS states is counterbalanced by a similar one on the ground state.

Excitation of the arrays in the UV, where the main chromophore is the Ir unit, leads to unexpected results. In the case of PH$_2$−Ir−PAu, the dissipation of the excited-state energy localized on the Ir complex (2.5 eV) occurs via energy transfer to both porphyrins. This is not the case in PZn−Ir−PAu, where the final product is again the CS state PZn$^+$−Ir−PAu$^-$ formed via a multistep electron-transfer mechanism such as the one illustrated in Figure 1d.[21]

Aromatic Amine/Naphthalene Diimide Arrays

A subsequent approach, aimed at increasing the distance between the extremities to enhance the CS lifetime, made use of the symmetric complex Ir(bzad−tpy)$_2$$^{3+}$ (Chart 3). In this case, we used typical organic donor and acceptor units, respectively, an aromatic amine (DAPA) and a naphthalene diimide (NDI) characterized by intense and clear spectroscopic signatures of their radical forms. Previously used porphyrins, in fact, because of the low molar absorption coefficients and the broad spectral features of the radicals extensively overlapping with the excited states, were liable to ambiguous results. In this case, the photosensitizer was the iridium complex, which could be selectively excited at wavelength >400 nm. The design follows the model in Figure 1d.
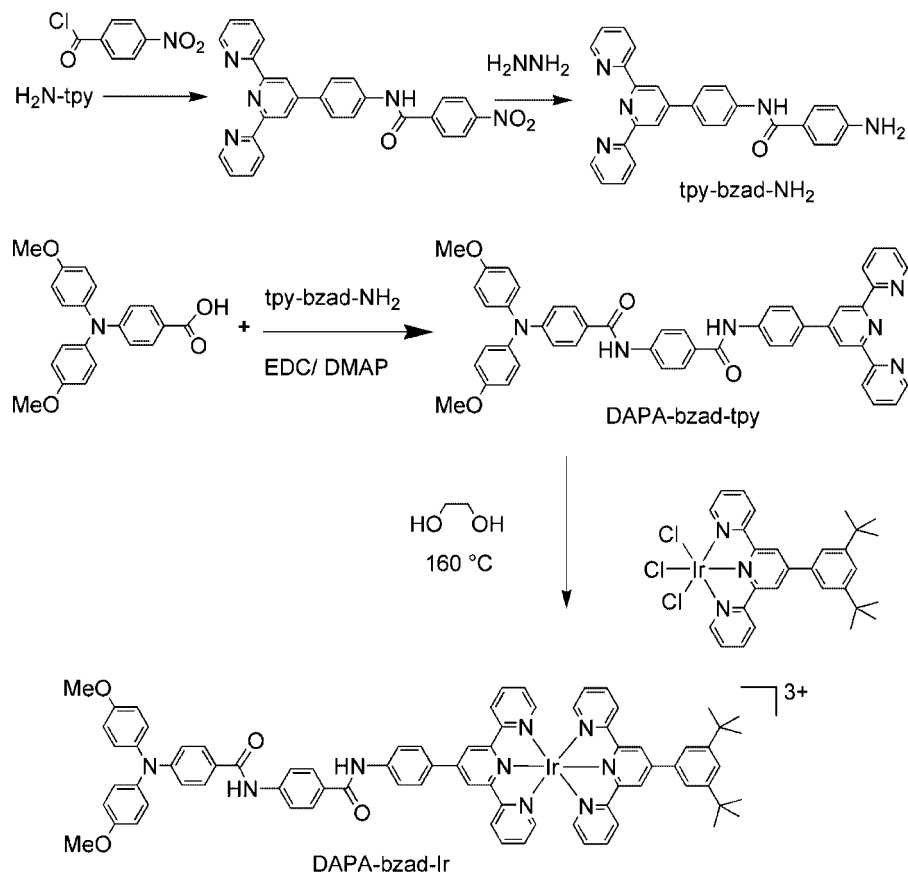
The synthetic strategy is reported in Charts 6 and 7. A method combining a modular as well as a "chemistry-on-the complex" approach has been used in relation to the chemical stability of the ligands in the usually harsh conditions required to substitute the iridium(III) coordination sphere. Starting from an iridium complex functionalized by an amine func-

CHART 7. Preparation of the Triad DAPA−Ir−NDI[a]

DAPA-Ir-NDI

[a] The last synthetic step is an organic reaction (amide bond formation) performed on an iridium precursor complex instead of a more classical complexation reaction of an already complete ligand.

tion, the dyads DAPA−Ir and Ir−NDI were prepared in a straightforward manner by reaction with 4-(*N,N*-bis(4-methoxyphenyl)amino)-methylbenzoyl chloride or *N*-(*p-t*Buphenyl)-*N*′-(*p*-benzoyl chloride)-naphtalene-1,8/4,5-tetracarboxydiimide (OCl-NDI) in 60% and 46% yield, respectively (Chart 6). The terpyridine DAPA−tpy bearing a triarylamine donor group linked to the tpy fragment by an amide bridge was prepared by a peptidic type coupling in the presence of *N,N*′-dimethylamino-4-pyridine (DMAP) and *N*-(3-dimethylaminopropyl)-*N*′-

ethylcarbodiimide hydrochloride (EDC). In the next step, the reaction of IrCl$_3$ with the DAPA−tpy in EtOH under reflux led to the intermediate DAPA−tpyIrCl$_3$ in low yield (30%). The experimental conditions of the coordination of the aminoterpyridine H$_2$N-tpy with DAPA−tpyIrCl$_3$ are very critical since the amino group undergoes partial degradation in ethylene glycol under reflux. A short reaction time at 160 °C is more favorable than prolonged heating. Purification of the crude material on TLC plates affords the intermediate DAPA−

CHART 8. Synthesis of the Dyad DAPA−bzad−Ir, Containing Two −Ph−NH−C(O)− Fragments in the Spacer

tpylrtpy−NH$_2$ in 42% yield. Eventually, the triad was obtained by reacting this intermediate with the acid chloride derivative OCl-NDI, obtained separately as an orange-yellow solid, leading to DAPA−Ir−NDI in 45% yield (Chart 7).

Due to the presence of amide bridges, behaving as "insulators" between the various components of the dyads and of the triad, the redox potentials observed for the couples DAPA$^+$/DAPA, NDI/NDI$^-$, and tpy/tpy$^-$ are virtually independent of the structure of the compound to which they belong, that is, ca. +0.76 V for oxidation of DAPA, ca. −0.5 V and −0.75 V for reduction of NDI and Ir, respectively (in CH$_3$CN vs SCE). A localized description of the states can therefore be used.

Excitation of the Ir component in the dyad DAPA−Ir leads to immediate quenching of the intense Ir luminescence and to the formation with 100% yield of a CS state (1.5 eV) living 70 ps characterized by a band at 765 nm, typical of DAPA$^+$.[22] Excitation of the DAPA moiety leads to the same CS state with 100% yield. In the dyad NDI−Ir, a slow energy transfer ($k = 4.2 \times 10^6$ s^{-1}) from the triplet localized on Ir (2.43 eV) to the triplet localized on A (2.06 eV) takes place.[23] Excitation of the NDI component to its lowest singlet excited state in the dyad NDI−Ir does not apparently lead to any intramolecular reac-

tivity (e.g., spin-forbidden energy transfer to NDI−^{3}Ir could be feasible), presumably for the intrinsic short lifetime of this state, 50 ps. Excitation of both Ir (and DAPA) units in the triad leads to the CS state DAPA$^+$−Ir$^-$−NDI, which evolves with a lifetime of 60 ps to the DAPA$^+$−Ir−NDI$^-$ charge-separated state (Scheme 2).

DAPA$^+$−Ir−NDI$^-$ stores 1.26 eV, is characterized by the DAPA$^+$ band at 765 nm and the NDI$^-$ bands at 475 and 610 nm, and decays slowly, on the hundreds of microseconds time scale (Figure 6).

Long-lived CS states and other intermediates (e.g., DAPA−Ir−^{3}NDI) can react intermolecularly with O$_2$ and with the ground-state DAPA−Ir−NDI, yielding arrays with a single radical site.[23] These, having to react diffusively with the array bearing the opposite charge, could live for very long times, and from the spectroscopic point of view are undistinguishable from intramolecular CS states. To exclude the contribution of intermolecular reactions, experiments at different concentration and laser intensity conditions have been conducted, confirming a lifetime of 120 μs in air-free and 100 μs in air-equilibrated solutions for the intramolecular recombination of the CS state.

While detailed experiments were performed on light intensity effects on DAPA−Ir−NDI, it became evident that under high light intensity the systems displayed a remarkable decrease of the lifetime and of the yield of the final CS state.[24] This was ascribed to multiple photon absorption in the same array, a rather common event in multichromophoric structures exposed to intense laboratory light sources. However under normal conditions, the results for this system are outstanding as far as lifetime and insensitivity to oxygen are concerned, but the yield of the CS state is rather low, on the order of 10%, due to the competition with ground-state recombination of the intermediate CS state DAPA$^+$−Ir$^-$−NDI (Scheme 2).

To improve the performances of the arrays, we reasoned that increasing the lifetime of the intermediate CS state DAPA$^+$−Ir$^-$−NDI should favor the formation of the final CS state DAPA$^+$−Ir−NDI$^-$. In this respect, decreasing the electronic coupling between the DAPA and Ir component by inserting a further benzamide group as in the dyad DAPA−bzad−Ir shown in Chart 8 should be a viable strategy. Obviously this could also imply a less efficient charge-separation step, but we could take the risk.

The dyad DAPA−bzad−Ir was prepared according to the reactions shown in Chart 8.[25] The terpyridine tpy−bzad-NH$_2$ was prepared in two steps by homologation of the already known 4′-(4-aminophenyl)-2,2′:2″-terpyridine with 4-nitrobenzoyl chloride followed by reduction of the nitro group with hydrazine in presence of catalytic amounts of palladium on charcoal. The terpyridine DAPA−bzad−tpy, bearing a triarylamine donor group linked to the tpy fragment by two amide bridges, was prepared by condensation of the terpyridine tpy−bzad-NH$_2$ with 4-(*N,N*-bis-(*p*-methoxy-phenyl)amino)-methylbenzoic acid, in presence of DMAP and EDC (peptidic coupling). The dyad DAPA−bzad−Ir was obtained in 70% yield by reaction of the precursor Ir(4′-(3,5-di-*tert*-butylphenyl)-2,2′:2″-terpyridine)Cl$_3$ with the terpyridine DAPA−bzad−tpy in ethylene glycol at 160 °C for 20 min.

The approach proved to be successful. In fact while the photoinduced charge separation is still very efficient (≥99%) in DAPA−bzad−Ir, the recombination of the resulting CS state is slowed by a factor of 3, to 210 ps.[25] This would imply that a new triad having one more benzamide group between DAPA and Ir with respect to DAPA−Ir−NDI can improve the yield of charge separation to ca. 35%. We are now working in this direction.

Conclusions and Perspectives

Several promising polyimine metal complexes have been proposed for light energy conversion applications as alternatives to the archetype Ru(bpy)$_3$$^{2+}$. Ir(tpy)$_2$$^{3+}$ is one of those, and because of the convenient linear arrangement of the substituents, the development of efficient synthetic procedures, and the outstanding photophysical and electrochemical properties, this complex has successfully been used as a component and assembling unit of multipartite arrays for producing charge separation.

Our groups have exploited the use of this complex both as electron relay and as photosensitizer, and with continuous improvements in the design of the arrays, we have achieved a system yielding a CS state with a lifetime of ca. 100 μs in air-equilibrated solutions and of ca. 120 μs in air-purged solutions. This is one of the most successful examples of charge separation based on a transition metal complex if we consider the lifetime and the stability in presence of air. We have recently identified a strategy to improve the relatively low charge separation yield by decreasing the electronic coupling between adjacent components. These results show the potential of Ir(tpy)$_2$$^{3+}$ in this application and the validity of the approach used, consisting of a pondered design of the array based on a detailed mechanistic study of the excitation energy dissipation processes.

BIOGRAPHICAL INFORMATION

Lucia Flamigni, born in 1949 in Romagna, Italy, received the Laurea in Chemistry at the University of Bologna in 1973. After postdoctoral experiences at the Universities of Manchester and Texas at Austin, she joined ISOF-CNR in Bologna where she is presently research director. Her main interest concerns photoinduced processes in multicomponent arrays.

Jean-Paul Collin was born in 1945 in Metz. After his Ph.D. in electrochemistry with Prof. J.-P. Schwing at Strasbourg University, he did postdoctoral work with Prof. J.-M. Lehn on water photolysis. He is now a CNRS research director. His present research interests concern photoinduced charge separation in multicomponent molecular systems and molecular machines.

Jean-Pierre Sauvage was born in 1944 in Paris. He is a CNRS director of research. His current interests span from models of the photosynthetic reaction center using transition metal complexes and porphyrins to topology (catenanes and knots) and molecular machines and motors. He is a member of the French Academy of Sciences.

REFERENCES

1 Wasielewski, M. R. Photoinduced electron transfer in supramolecular systems for artificial photosynthesis. *Chem. Rev.* **1992**, *92*, 435–461.

2 Gust, D.; Moore, T. A.; Moore, A. L. Mimicking photosynthetic solar energy transduction. *Acc. Chem. Res.* **2001**, *34*, 40–48.

3 Lehn, J.-M.; Sauvage, J.-P. Photoinduced reduction and oxidation of water-recent advances in the generation of hydrogen and oxygen by visible-light irradiation of aqueous-solutions. *Nouv. J. Chim.* **1977**, *1*, 449–451.

4 Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. Hydrogen evolution from water by visible-light, a homogeneous three component test system for redox catalysis. *Helv. Chim. Acta* **1978**, *61*, 2720–2730.

5 Du, P.; Schneider, J.; Jarosz, P.; Eisenberg, R. Photocatalytic generation of hydrogen from water using a platinum(II) terpyridyl acetylide chromophore. *J. Am. Chem. Soc.* **2006**, *128*, 7726–7727.

6 Chakraborty, S.; Wadas, T. J.; Hester, H.; Schmehl, R.; Eisemberg, R. Platinum chromophore-based systems for photoinduced charge separation: A molecular design approach for artificial photosynthesis. *Inorg. Chem.* **2005**, *44*, 6865–6878.

7 Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. Chemical approaches to artificial photosynthesis. 2. *Inorg. Chem.* **2005**, *44*, 6802–6827.

8 Balzani, V.; Clemente-Leon, M.; Credi, A.; Ferrer, B.; Venturi, M.; Flood, A. H.; Stoddart, J. F. Autonomous artificial nanomotor powered by sunlight. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 1178–1183.

9 Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. Photochemically induced charge separation at the molecular level. A chromophore quencher complex containing both an electron transfer donor and an acceptor. *J. Am. Chem. Soc.* **1987**, *109*, 2519–2520.

10 Borgström, M.; Shaikh, N.; Johansson, O.; Anderlund, M. F.; Styring, S.; Akermark, B.; Magnuson, A.; Hammarström, L. Light induced manganese oxidation and long-lived charge separation in a $Mn_2^{II,II}$-$Ru(bpy)_3$-acceptor triad. *J. Am. Chem. Soc.* **2005**, *127*, 17504–17515.

11 Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Decola, L.; Flamigni, L.; Balzani, V. Photoinduced processes in dyads and triads containing a ruthenium(II)-bis(terpyridine) photosensitizer covalently linked to electron donor and acceptor groups. *Inorg. Chem.* **1991**, *30*, 4230–4238.

12 Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Decola, L.; Flamigni, L.; Balzani, V. Photoinduced processes in dyads and triads: An osmium (II)-bis(terpyridine) photosensitizer covalently linked to electron donor and acceptor groups. *Inorg. Chem.* **1992**, *31*, 4112–4117.

13 Harriman, A.; Odobel, F.; Sauvage, J.-P. Multistep electron transfer between porphyrin modules assembled around a ruthenium center. *J. Am. Chem. Soc.* **1995**, *117*, 9461–9472.

14 Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. Photoinduced processes in highly coupled multicomponent arrays based on a ruthenium(II)bis(terpyridine) complex and porphyrins. *Chem.—Eur. J.* **1998**, *9*, 1744–1754.

15 Flamigni, L.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. Photochemistry and photophysics of coordination compounds: Iridium. *Top. Curr. Chem.* **2007**, *281*, 143–203.

16 Collin, J.-P.; Dixon, I. M.; Sauvage, J.-P.; Williams, J. A. G.; Barigelletti, F.; Flamigni, L. Synthesis and photophysical properties of iridium(III) bisterpyridine and its homologues. A family of complexes with a long-lived excited state. *J. Am. Chem. Soc.* **1999**, *121*, 5009–5016.

17 Flamigni, L.; Ventura, B.; Barigelletti, F.; Baranoff, E.; Collin, J.-P.; Sauvage, J.-P. Luminescent iridium(III)-terpyridine complexes. Interplay of ligand centred and charge transfer states. *Eur. J. Inorg. Chem.* **2005**, 1312–1318.

18 Ayala, N. P.; Flynn, C.M., Jr.; Sacksteder, L.A.; Demas, J. N.; DeGraff, B. A. Synthesis, luminescence, and excited-state complexes of the tris(1,10-phenanthroline)- and bis(terpyridine)iridium(III) cations. *J. Am. Chem. Soc.* **1990**, *112*, 3837–3844.

19 Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Barigelleti, F.; Flamigni, L. Charge separation in a molecular triad consisting of an Ir(III)-bis-terpy central core and porphyrins as terminal electron donor and acceptor groups. *Angew. Chem., Int. Ed.* **2000**, *39*, 1292–1295.

20 Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L. Porphyrinic dyads and triads assembled around iridium(III) bis-terpyridine: Photoinduced electron transfer processes. *Inorg. Chem.* **2001**, *40*, 5507–5517.

21 Flamigni, L.; Marconi, G.; Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P. Switching of electron-to energy-transfer by selective excitation of different chromophores in arrays based on porphyrins and a polypyridyl iridium complex. *J. Phys. Chem. B* **2002**, *106*, 6663–6671.

22 Baranoff, E.; Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Ventura, B.; Flamigni, L. Dyads containing iridium(III) bis-terpyridine center: Synthesis and electron transfer study. *Inorg. Chem.* **2004**, *43*, 3057–3066.

23 Flamigni, L.; Baranoff, E.; Collin, J.-P.; Sauvage, J.-P. A triad based on an iridium(III) bisterpyridine complex leading to a charge-separated state with a 120 μs lifetime at room temperature. *Chem.—Eur. J.* **2006**, *12*, 6592–6606.

24 Flamigni, L.; Baranoff, E.; Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Ventura, B. Light intensity effects on photoinduced charge separation parameters in a molecular triad based on an iridium(III) bis(terpyridine) unit. *ChemPhysChem* **2007**, *8*, 1943–1949.

25 Flamigni, L.; Ventura, B.; Baranoff, E.; Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P. A triphenylamine/bis(terpyridine)Ir^{III} dyad for the assembly of charge-separation constructs with improved performances. *Eur. J. Inorg. Chem.* **2007**, 5189–5198.