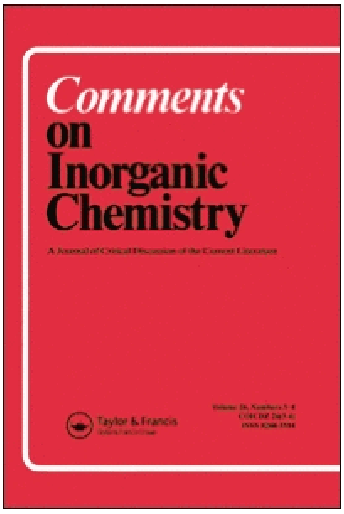

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METAL COMPLEXES FOR MOLECULAR ELECTRONICS AND PHOTONICS

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Within the fields of coordination and organometallic chemistry there has recently been much interest in the design, synthesis and study of novel complexes having potential for applications in the nascent technologies of molecular electronics and photonics. Here we provide an overview of the current status of research involving organotransition metal complexes in the following important areas: liquid crystalline materials, nonlinear optical materials, molecular wires and switches, chromophore-quencher complexes, dye-sensitized photovoltaic cells and organic light-emitting diodes. Coverage is selective, generally focusing on highlights and the most recent developments, with the broad aim of conveying the essence and excitement of a group of related research topics at the forefront of modern inorganic chemistry.

1. INTRODUCTION

Coordination and organometallic complexes of transition metals have for many years found widespread uses in homogeneous catalysis and also niche applications in other areas such as metallopharmaceuticals. However, recent interest in the emerging sciences of molecular electronics and photonics has inspired many studies with metal complexes as the basis of potential new functional materials. The well-documented inherent limitations of current semiconductor-based electronic devices

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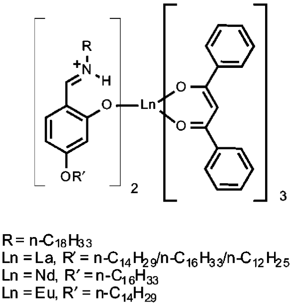
in terms of both speed and scale of operation are the principle motivation behind much molecular electronics and photonics research. Such investigations can involve either the exploitation of the bulk properties of molecular materials or the tantalizing longer-term prospect of using molecular-scale devices for electronic and/or photonic data processing. From both of these perspectives, organotransition metal complexes offer many exciting possibilities due to their diverse structural, electronic and optical properties.

In this review, we describe the current state of the art relating to the development of organotransition metal complexes in a range of important fields, *i.e.* liquid crystalline materials, nonlinear optical materials, molecular wires and switches, chromophore-quencher complexes, dye-sensitised photovoltaic cells and organic light-emitting diodes. Each of these particular areas has been reviewed thoroughly on several previous occasions, but concise works which deal with all of these topics together are rare. Our coverage is obviously somewhat subjective and heavily selective, but the overall aim is to convey the essence and excitement of much recent and current research. References more than 5 years old (*i.e.* prior to 1999) are only included in a few instances. Each of the topics chosen for discussion is very broad, so we will focus on highlights and especially the most recent developments. The relative lengths of the different sections reflect to some extent the level of very recent publishing activity. Although they might reasonably be included in a broad definition of molecular electronics and photonics, molecular magnetic materials (an area sometimes given the label "spintronics") are specifically excluded from the present work.

2. METAL-CONTAINING LIQUID CRYSTALS

The properties of liquid crystalline materials make them particularly useful for photonic applications.[1] The liquid crystalline state, or mesophase, lies between the crystalline and liquid phases in terms of order, and liquid crystals may be considered as fluids with long-range anisotropy. Mesophases are classified according to the degree and type of order which they exhibit. For example, nematic mesophases have orientational but not positional order, while smectic mesophases have layered structures. Manipulation of the long-range anisotropy by external magnetic, optical or electronic fields leads to optical effects that may be exploited in applications such as liquid crystal displays (LCDs).[2] Liquid crystalline metal complexes, also known as metallomesogens, are potentially important for two reasons. Firstly, the introduction of metal center(s) may lead to new magnetic, photophysical and/or electronic properties. Secondly, the metal may strongly influence the structure and orientation in the mesophase. Because metallomesogens have been the subject of several very recent reviews,[3] but the number of reports in the last few years is not overly large, discussion here is kept relatively brief.

Trivalent lanthanide (Ln) ions have been especially thoroughly studied in the search for metallomesogens with new properties.[3c] Most such ions are paramagnetic with high magnetic moments, which may allow magnetic switching of the mesophase orientation, possibly leading to applications in magneto-optical data storage. Also, a number of Ln^{III} ions exhibit intense visible luminescence, which could be exploited to produce emissive LCDs. Binnemans and co-workers have reported the synthesis of high coordination number liquid crystalline tris-β-diketonatolanthanide(III) complexes.[4,5] The first such complexes **(1)** have the formula $[Ln(bdm)_3L_2]$ where Ln = La, Nd or Eu; dbm = 1,3-diphenyl-1,3-propanedione and L is a monodentate Schiff-base, *N*-alkyl-4-alkyloxy-2-hydroxy-benzaldimine.[4] Following this work, complexes of the type $[Ln\{(RO)_2bdm\}_3(L\text{–}L)]$ were reported **(2)** Ln = Tb or Eu; $(RO)_2dbm$ is a *para*-alkoxy-substituted 1,3-diphenyl-1,3-propanedione and L–L is an α-diimine such as 1,10-phenanthroline (phen), 2,2′-bipyridyl (bpy) or 5,5′-substituted bpy).[5] The key difference between these two types of Ln^{III} complex is that in the second case the mesomorphism is introduced by the β-diketonate ligand itself rather than by the ancillary ligand. Both types of complex form smectic mesophases on cooling from a melt, and those of the α-diimine complexes have greater thermal



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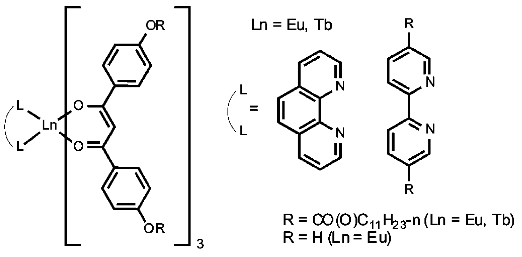

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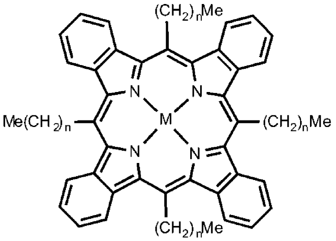
stability. Furthermore, the Eu^{III} α-diimine complexes show characteristic intense red emissions from the vitrified mesophases.

Various d-block transition metals have also been used to impart new properties to liquid crystals. For example, Chan and co-workers have prepared bpy-containing polyamides by condensation of 2,2′-bipyridyl-5-5′-dicarboxylic acid with a range of diamines.[6] Of these, the flexible polyamides have thermotropic liquid crystalline properties, while the more rigid ones give lyotropic mesophases when dissolved in suitable solvents. Polymeric Ru^{II} complexes were prepared either by direct complexation of the bpy-containing polyamide, or by polymerization of Ru^{II}-containing monomers. The alignment of the molecules in the mesophase is disturbed by the bulky Ru^{II} centers, such that only polymers with a low metal loading (below 50%) show lyotropic mesophases. The complexes show red metal-to-ligand charge-transfer (MLCT) emissions at *ca* 700 nm and have been incorporated into thin-layer light-emitting devices (see also section 7 below).

Porphyrin complexes have also been exploited as metallomesogens. Shimizu and co-workers have compared the properties of a liquid crystalline tetraphenylporphyrin oxovanadium(IV) complex with those of the free-base porphyrin.[7] These compounds were sandwiched between indium-tin oxide (ITO)-coated glass electrodes and their photoconductivity measured. The photocurrent observed with the metallated porphyrin is approximately two orders of magnitude higher than with the free-base analogue. Qi and Liu have reported the liquid crystalline properties of tetraalkyl tetrabenzoporphyrin and its $Mn^{III}Cl$, Ni^{II} and Cu^{II} complexes (**3**).[8] All of these materials exhibit hexagonal columnar (col_h) mesophases at room temperature and are *p*-type semiconductors, as indicated by surface photovoltage spectroscopy. These compounds also all show fluorescence, and at low temperatures the metal complexes exhibit phosphorescence at 725 nm.

Because the photonic properties of liquid crystals depend on the alignment of molecules, structural control at the molecular level is of key importance. Fanizzi and co-workers have prepared the first enantiomerically pure liquid crystalline complexes with the chiral center directly bound to the metal (**4**).[9] These complexes consist of a Pt^{II} dichloride stilbazole center bearing a chiral sulfoxide ligand. Interestingly, a difference in thermal behavior between the racemic and enantiomerically pure forms is observed: both forms exhibit smectic F mesophases, but the racemic forms also have a more ordered crystal smectic G phase at lower temperatures.



M = Cu, Ni, MnCl
n = 5, 7, 9, 11, 13, 15, 17

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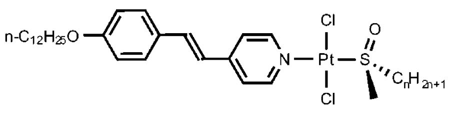


n = 14–16

4

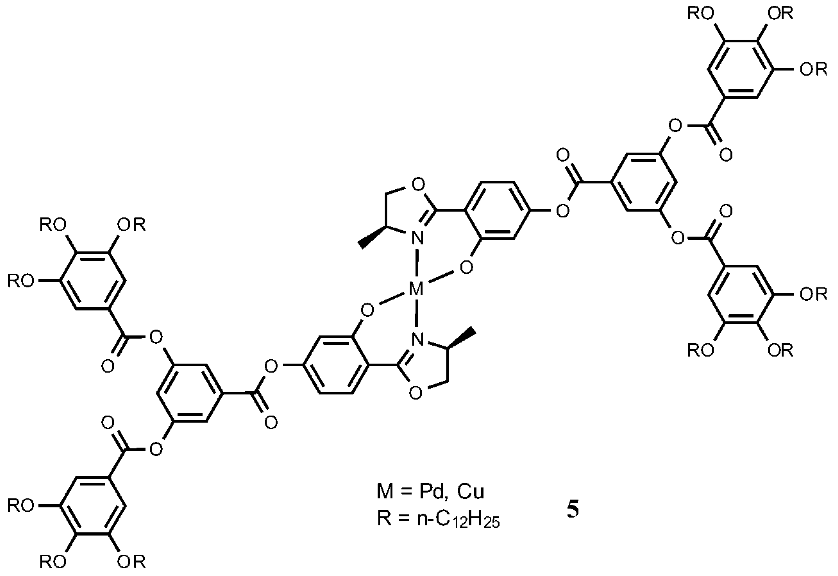
Work by Ziessel and co-workers has focused on liquid-crystalline Cu^{I} complexes.[10] In particular, binuclear helical complexes of bpy[11] and 2,2′:6′,″-terpyridyl (tpy)[12] Schiff-base ligands have been reported. Notably, these complexes are liquid crystalline at room temperature. A more recent report describes a wedge-shaped Cu^{I} complex that forms a hexagonal columnar mesophase.[13] The number of molecules in a length of column equal to the molecular thickness is temperature dependent, *i.e.* eight molecules at 40°C and six at 120°C.

A particularly significant report by Serrano and co-workers describes the careful design of metal complexes which form helical columnar mesophases (**5**).[14] Pd^{II} and Cu^{II} complexes of oxazoline-derived ligands were prepared, which have stereogenic centers in the coordination environment of the metal. This chirality is transferred to the mesophase, which consists of stacks of molecules that rotate with respect to one another along the column. One full helical turn occurs every six molecules, and the *S*-isomer of the ligand leads to left-handed helices, whilst right-handed helices are formed with complexes of the *R*-ligand.

3. COMPLEXES FOR NONLINEAR OPTICS

Nonlinear optical (NLO) materials are of great technological importance in areas such as optical data processing and storage. Molecular organic materials,[15] including organotransition metal complexes,[16] have been extensively investigated as potential alternatives to the traditional inorganics such as lithium niobate ($LiNbO_3$). Metal complexes often exhibit intense charge-transfer transitions associated with large molecular NLO responses, and are especially attractive for the creation of multifunctional materials due to their structural and electronic diversity. This field is still relatively young, so most studies to date have focused on chromophore design and the derivation of molecular structure-activity correlations for both quadratic and cubic NLO effects. The former are generally characterized by first hyperpolarizabilities β, and the latter by second hyperpolarizabilities γ and bulk susceptibilities $\chi^{(3)}$.

Complexes of electron-donating ferrocenyl (Fc) and related organometallic units with η^5-cyclopentadienyl (Cp) ligands are popular subjects for NLO studies. Recent highlights include the work of Farrell *et al.* who have used hyper-Rayleigh scattering (HRS) experiments to determine β values for Fc polyenes with azulenylium or guaiazulenylium electron acceptors (*e.g.* **6**)[17a] and complexes with $[(CpFeCO)_2(\mu{-}CO)(\mu{-}C{=}CH{-})]$ donors and azulenylium acceptors.[17b] Chiffre *et al.* have achieved the highest yet second harmonic generation (SHG) efficiency for a 2-(4-nitrophenyl)ethenylferrocene of 140 times that of urea with a 1907 nm laser, which arises from a perfect dipolar alignment in the noncentrosymmetric space group *P*1.[18] In rare examples of cubic NLO studies on Fc derivatives, heterotri- and tetranuclear complexes of pyridyl-coordinated Zn^{II}, Cd^{II} or Hg^{II} centers[19] and conjugates with oxasmaragdyrin or oxacorrole macrocycles[20] have been investigated *via* *Z*-scan measurements.



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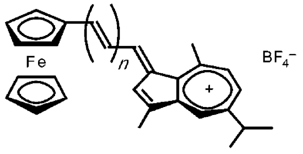
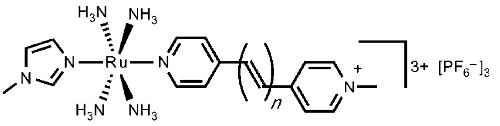


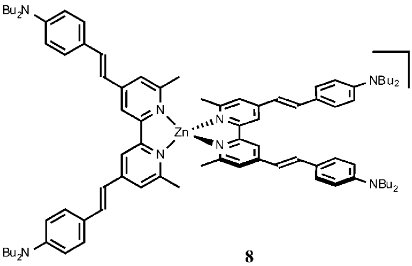
n = 0–3 **6**



n = 0–3 **7**

Complexes of monodentate pyridyl ligands have been extensively investigated for their NLO properties. The Ru^{II} ammine salts studied by Coe *et al.* have very large static first hyperpolarizabilities β_0 ($>500 \times 10^{-30}$ esu) and notably provide the first examples of redox-switchable molecular NLO responses,[21] a phenomenon which has since been demonstrated for both quadratic and cubic effects in other complexes.[22] Coe and colleagues have also applied HRS and electroabsorption (Stark) spectroscopy to polyene species (*e.g.* **7**) which show highly unusual optical behavior in that their MLCT bands blue-shift and β_0 decreases as the conjugated chain extends beyond $n = 2$.[23] Interestingly, electric-field induced SHG (EFISHG) studies by Tessore *et al.* have shown a marked concentration-dependence of β in tetrahedral Zn^{II} pyridyl complexes on replacing acetate by triflate co-ligands.[24] Various coordination polymers of metal ions such as Zn^{II}, Cd^{II}, Hg^{II} or Pb^{II} with bridging pyridyl or related *N*-heterocyclic ligands combine SHG with visible transparency,[25] and also substantial cubic NLO effects, as probed by the *Z*-scan technique.[26] Han *et al.* have reported an SHG-active and fluorescent Zn^{II} coordination network bridged *via* 4-sulfanylmethyl-4′-phenylcarboxylate pyridine with two types of homo-chiral helices.[27]

Derivatives of $[Ru^{II}(bpy)_3]^{2+}$ (RTB) and related octopolar tris-chelates show interesting quadratic NLO properties. Materials-orientated work with RTB-based systems has involved a highly thermally stable polyimide derivative[28a] and also a dendrimer containing 7 complex units.[28b,c] The larger β response of the latter when compared with the linear polymer containing an average of 14 chromophores is attributable to quasi-optimized octopolar ordering in the dendrimer.[28b,c] HRS-based data for Zn^{II} complexes show that β_0 increases monotonically with the number of coordinated bpy ligands, as the chromophore structure changes from dipolar to D_{2d} (**8**) and then D_3 octopolar.[29] Fave *et al.* have applied HRS to some unusual Pd^{II} complexes of chelating



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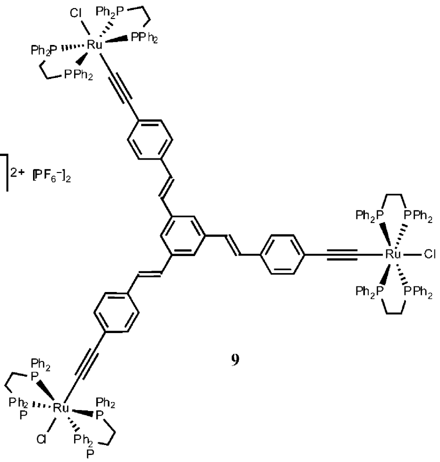

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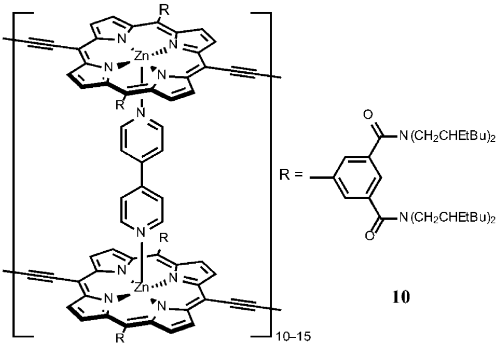
pyridyl-phosphole ligands in which trans-effects are cleverly used to generate a favourable dipolar molecular structure.[30] The cubic NLO properties of trinuclear Ru^{II} tris-(α-diimine) complexes have also been investigated *via* *Z*-scan,[31] affording reasonably large γ values, and tpy-based complexes of Ru^{II}, Os^{II}, Zn^{II}, Ru^{III} and Ir^{III} also show both quadratic and cubic NLO effects.[32,33]

Complexes of σ-bonded acetylide ligands have also been well-investigated for their NLO properties, especially by Humphrey and co-workers.[34] Such studies have recently involved both quadratic (HRS) and cubic (*Z*-scan/electroabsorption) NLO measurements on dipolar and C_3 octopolar (*e.g.* **9**) stilbenylethynyl Ru^{II} complexes which show "dimensional evolution" of NLO responses.[34a] *Z*-scan has also been applied to heterotrinuclear Fc-linked Au^I and Ru^{II} complexes,[34b] and HRS and TD-DFT studies with dipolar Fe^{II}, Ru^{II} and Os^{II} complexes indicate that β increases with the π-donating ability of the metal center.[34c] Work by Humphrey and colleagues has also focused on redox-switching of quadratic and cubic NLO responses in Ru^{II} complexes.[22c] Studies by Garcia *et al.* on Fe^{II} σ-acetylides indicate that such complexes have larger NLO responses than their Ru^{II} analogues, attributable to the greater electron-richness of the first row metal.[35]

Extensive delocalized π-systems render complexes of porphyrin, phthalocyanine and related ligands especially attractive for cubic NLO effects, optical limiting (OL) applications being a strong possibility.



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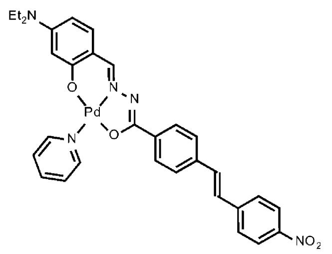

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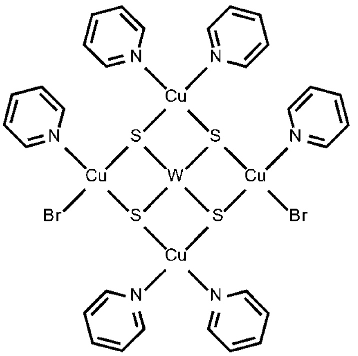
Time-resolved optical Kerr effect measurements on self-assembled oligomeric Zn^{II} porphyrins by Ogawa *et al.* yield very large off-resonant cubic optical non-linearities, with γ increasing markedly with the chain length.[36] Oligomeric "ladder" Zn^{II} porphyrins (**10**) have also been investigated by Anderson and co-workers, degenerate four-wave mixing (DFWM) data revealing amplified $\chi^{(3)}$ responses.[37] HRS studies by Uyeda *et al.* on Zn^{II} porphyrins linked to $[M^{II}(tpy)_2]^{2+}$ (M = Ru or Os) units reveal unusual frequency dispersion effects of β,[38] whilst *Z*-scan experiments with In^{III} porphyrins indicate that the NLO absorption is enhanced by axial coordination of osmium carbonyl clusters.[39] The promising OL behavior of axially-substituted In^{III} or Ga^{III} phthalocyanines has been investigated by Hanack and co-workers,[40] and this technologically important field has been recently reviewed.[41]

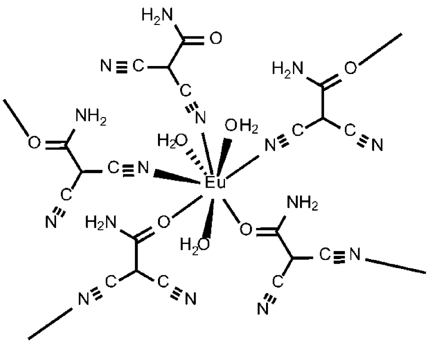
Di Bella and Fragalà have reported systematic ZINDO calculations on Ni^{II} Schiff base complexes with large off-diagonal components of β,[42] and EFISHG studies by Cariati *et al.* on pyridine adducts of Cu^{II} and Pd^{II} complexes of *N*-salicylidene-*N*′-aroylhydrazine ligands (*e.g.* **11**) afford very large $\mu\beta$ (μ = dipole moment) values.[43] Infinite 3-D network complexes such as $Zn^{II}Cd^{II}(SCN)_4$ combine bulk quadratic NLO activity with visible transparency and are hence promising materials for UV SHG.[44] Complexes of 1,2-dithiolene (DT) and related ligands have attracted considerable attention for their NLO properties, especially cubic effects. The OL properties of neutral Ni^{II} DTs have been investigated by Tan *et al.*,[45] whilst Dai *et al.* have applied DFWM to tetrahedral Zn^{II} or Cd^{II} complexes.[46] The quadratic NLO properties of Ni^{II} DTs were studied by Bigoli *et al.* using solvatochromically-determined dipole moment changes to estimate β_0 according to the two-state model,[47] and TD-DFT has been used to derive β_0 values for Ni^{II}, Pd^{II} or Pt^{II} DTs.[48]

Many studies have addressed the cubic NLO and OL properties of metal cluster complexes with various topologies, such as salts of anionic cubic clusters $[Et_4N]_3[MOS_3(\mu_3\text{-}I)(AgI)_3]$ (M = Mo/W)[49] and heterotrimetallic phosphine-capped linear clusters.[50] Planar "open" heterothiometallic clusters, $M^{VI}S_4Cu^{I}{}_4X_2(py)_6$ (M = Mo/W; X = Cl/Br/I, py = pyridine; *e.g.* **12**), show superior OL properties when compared with those of the benchmark material C_{60}, even on an ultrafast timescale.[51] Impressive OL properties are also exhibited by cluster polymers such as the 3-D cross-framework compound $\{[NEt_4]_2[W^{VI}Se_4Cu^{I}{}_4(CN)_4]\}_n$, which contains pentanuclear planar clusters.[52] Zhang *et al.* have reported efficient OL from an unusual polyicosahedral cluster $Ag_{20}Cl_{14}Au_{18}(PPh_3)_{12}$, in doped PMMA thin films.[53]

The strongly luminescent, 2-D sheet coordination polymer $\{[Eu^{III}(cda)_3(H_2O)_3]\cdot H_2O\}_\infty$ (**13**, cda = carbamyldicyanomethanide anion) provides a rare example of an Ln-based NLO material, which crystallizes non-centrosymmetrically and combines a high SHG activity with good visible transparency.[54] Xie *et al.* have reported 2-D chiral $\{U^{VI}O_2\}^{2+}$ coordination polymers which show modest SHG activities and also ferroelectric behavior in one case.[55] *Z*-scan studies carried out by Hou *et al.* on some interesting octameric ellipsoidal complexes of La^{III} or Ce^{III} reveal contrasting NLO absorptive and refractive behavior.[56]



12 (W ion is tetrahedrally coordinated)

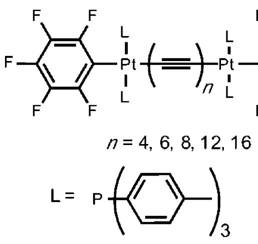


13 (portion of sheet structure)

4. MOLECULAR WIRES AND SWITCHES

There is widespread current interest in compounds that might behave as components in nanoscale electronic or photonic devices. In particular, pseudo one-dimensional molecules that are capable of electronic transport between redox-active metal centers have been widely studied.[57] Such "molecular wires" fall broadly into two categories: complexes where two or more metal centers are linked by a conjugated organic bridge, and those containing metal-metal bonds supported or unsupported by bridging ligands. A wider definition might also include metal-containing conducting polymers[58] and metal-functionalized DNA.[59]

Perhaps the most interesting and widely studied ligand-bridged complexes contain metal centers linked by linear elemental carbon chains (C_x where $x \geq 2$).[57a,60] Gladysz and co-workers have reported a series of polyalkyne-bridged dinuclear Re^I complexes, ReC_xRe ($Re = \{Cp^* Re(NO)(PPh_3)\}^+$, $Cp^* = \eta^5\text{-}C_5Me_5$; $x = 4\text{–}20$).[61] With increasing chain length, the visible absorptions become red-shifted and gain intensity, and the separation between the first and second reduction potentials (from cyclic voltammetry) decreases. The complex $ReC_{20}Re$ exhibits only a single oxidation process, and may be considered the point at which the two metal centers behave electrochemically independently. Further studies by Gladysz and co-workers describe the preparation and structural characterization of dinuclear Pt^{II} complexes $[(C_6F_5)\{P(C_6H_4\text{-}4\text{-}Me)_3\}_2Pt]_2C_x$ where $x = 4, 6, 8, 12$ or 16 (**14**).[62] The crystal structure of the C_{12} complex shows very pronounced curvature of the carbon chain, whilst the C_{16} complex is surprisingly straighter than its C_{12} counterpart in the solid state, having a slight S-shape. Despite their curvature, all of these complexes are highly stable, with decomposition temperatures between 234 and 288°C. Other very recent related reports involve luminescent



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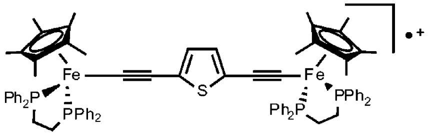

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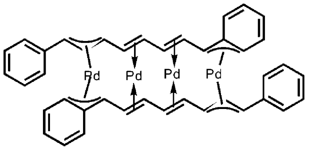
Pt^{II}(4,4′,4″-tri-*tert*-butyl-tpy) species[63] and detailed TD-DFT studies on Fe^{II} and Re^{I} complexes with butadiyndiyl bridges.[64]

Since the preparation of extended C_x chains can be challenging, alternative related bridging units have also attracted attention. For example, Lapinte and co-workers have compared the properties of mixed-valence complexes [Cp*(dppe)Fe(C≡C-X-C≡C)Fe(dppe)Cp*] where X is a 2,5-thiophenyl (**15**) or butadiyndiyl spacer.[65] Notably, the inclusion of the thiophenyl spacer greatly facilitates the synthesis of the complex without affecting the extent of electronic conduction. Hong and co-workers have prepared a series of dyads based on *cis*-$\{M^{II}(bpy)_2Cl\}^+$ (M = Ru or Os) units linked by diphosphines $Ph_2PC{\equiv}CPPh_2$ (C_2P_2) and $Ph_2PC{\equiv}CC{\equiv}CPPh_2$ (C_4P_2).[66] Electrochemical studies on these homobinuclear complexes unsurprisingly show that the shorter bridge C_2P_2 permits stronger metal-metal electronic communication than does the longer C_4P_2 unit. These heterodinuclear complexes show fast photoinduced Ru^{II} to Os^{II} energy-transfer that occurs *via* the Dexter (double electron exchange) mechanism. Another photoactive molecular wire based on Ru^{II} polypyridyls has been reported by Shiotsuka *et al.*[67] This trinuclear complex contains a Au^{I} bis(acetylide) center with terminal $\{Ru^{II}(bpy)_2(phen)\}^{2+}$ units, and undergoes 95% efficient Au^{I} to Ru^{II} energy-transfer.

An interesting variation on polyacetylide-bridged complexes is provided by polyynes containing metal-metal bonded spacers.[68,69] A pioneering study by Lehn and co-workers involves a tetranuclear complex containing two $Ru_2(dpf)_4$ units (dpf = N,N′-diphenylformamidine) linked by a bis(acetylide) bridge.[69] The crystal structure of this complex shows a partially bent structure in which the phenyl groups of the dpf ligands provide an insulating sheath, protecting the conjugated chain. Electrochemical analysis indicates predictably strong electronic delocalization within the molecule.

High nuclearity metal-metal bonded chains are also important synthetic targets in the search for molecular wires. Jiang *et al.* describe the synthesis of an air-stable chain of five osmium atoms unsupported by bridging ligands, $Os_5(CO)_{18}(CNBu^t)_2Cl_2$,[70] which is almost linear and contains strong Os–Os single bonds. An interesting study by Tejel *et al.* concerns a hexanuclear iridium complex, $Ir_6(\mu\text{-}OPy)_6I_2(CO)_{12}$ (OPy = 2-pyridonate),[71] which is made up of a nearly linear metal-metal bonded chain of Ir atoms in oxidation state +1.33. Murahashi, Kurosawa and co-workers have combined metal-metal bonded chains with conjugated organic molecules in a series of organometallic sandwich complexes.[72] These complexes comprise two conjugated



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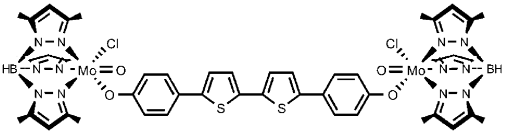

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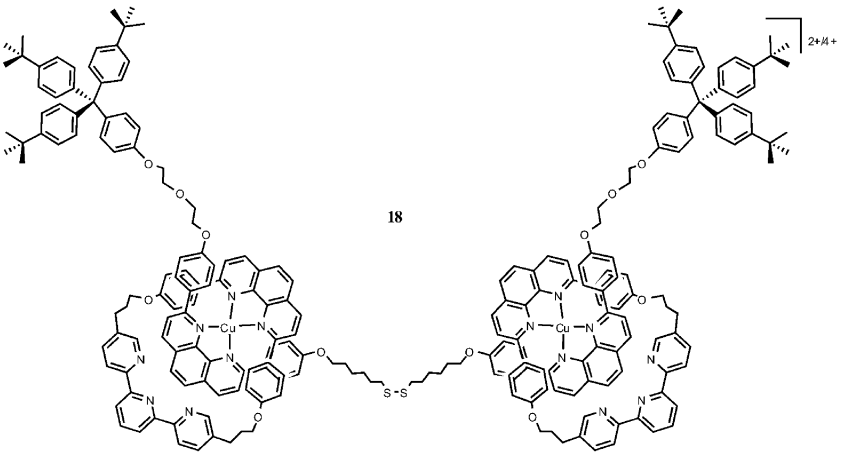
polyenes, $-(CH)_m-$, sandwiching a palladium chain Pd_n^{2+}. A tetranuclear complex $[Pd_4(\mu\text{-}\eta^3{:}\eta^2{:}\eta^2{:}\eta^3\text{-1,8-diphenylocta-1,3,5,7-tetraene})_2]^{2+}$ (**16**) was prepared by reaction of $[Pd(CH_3CN)_4]^{2+}$and $Pd_2(dba)_3$ (dba = dibenzylideneacetone) with the polyene, whilst a subsequent report describes an alternative preparation using $[Pd_2(CH_3CN)_6]^{2+}$.[73]

Metal complexes with electrochemically or photochemically switchable properties are of interest as components of molecular devices.[74] For example, compounds with electrochromic near infrared (NIR) absorptions have potential for communications and data storage applications.[75] Ward and co-workers have studied a range of electrochromic NIR dyes based on molybdenum and ruthenium.[76] A notable example is a bridged dinuclear oxomolybdenum(V) complex $\{MoCl(O)Tp^*\}_2L$ (**17**, L = $\{4,4'\text{-}OC_6H_4(2,5\text{-}C_4H_2S)_2C_6H_4O\}^{2-}$, Tp* = hydrotris(3,5-dimethylpyrazolyl)borate).[77] UV/Vis/NIR spectroelectrochemistry shows that the neutral starting Mo(V)/Mo(VI) complex is transparent in the NIR region, whereas the oxidized Mo(V)/Mo(VI) species has a strong absorption maximum at 1340 nm. An optically transparent thin-layer electrode (OTTLE) cell was used to monitor the NIR absorbance as the applied potential was stepped between 0 and 1.5 V, and the absorbance was reversibly switched over several thousand cycles. The complex behaves as a variable optical attenuator (VOA), since the optical power of a 1300 nm laser passed through a solution of the complex varies as a function of the applied voltage.

Another class of redox-active molecular switches has been termed "molecular machines", *i.e.* catenanes and rotaxanes where the interlocked molecular components move with respect to one another in response to an electrochemical stimulus.[78] Sauvage and co-workers have described a copper rotaxane (**18**) comprising an axis with two bidentate ligands; and two wheels, each containing one bidentate and one tridentate ligand.[79] The two complexed copper ions can be tetra- or pentacoordinated. Rotation of the wheels about the axis is achieved electrochemically since



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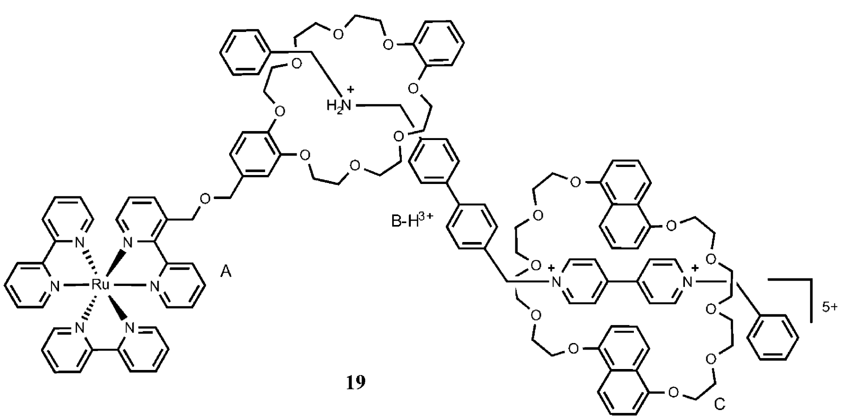
Cu^{I} is more stable when four coordinate, whilst the five-coordinate configuration is favored with Cu^{II}. The axes have central disulfide bridges which allow the rotaxanes to be adsorbed onto the surface of gold electrodes *via* Au–S bonds.

MacDonald, McGimpsey and co-workers have also investigated the photoswitchable properties of copper complexes self-assembled onto gold surfaces.[80,81] 300 nm irradiation of a Cu^{II} complex of 2,2′-dipyridylethylene results in irreversible conversion of the ligand from the chelating cis isomer to the trans form, which is unable to form a bidentate complex.[81] Contact angle measurements reveal a difference in surface wettability between the cis and trans adsorbed species, with the cis isomer giving a more hydrophobic surface. The authors are currently investigating the use of such photochromic molecules to provide reversible switching of wettability, which is of interest in the field of nanofluidics.

5. CHROMOPHORE-QUENCHER COMPLEXES

The interaction of sunlight with biological systems is responsible for many important natural processes such as photosynthesis. An important target for synthetic chemists is the creation of photochemical molecular devices (PMDs) capable of performing related useful functions such as the conversion of sunlight into electrical or chemical energy.[82] Chromophore-quencher (CQ) systems based on organotransition metal



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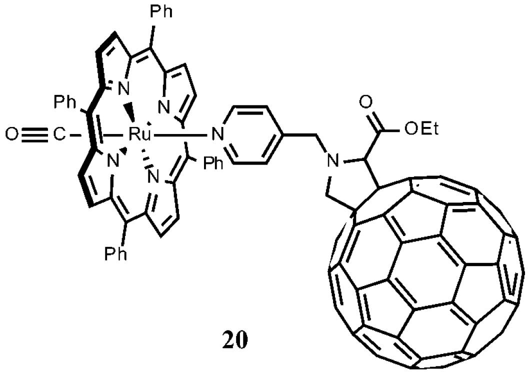
complexes have been widely exploited in this field, most being derivatives of metal polypyridyls or metalloporphyrins.[83] Such complexes have low energy excited states that may be quenched by energy or electron-transfer. A primary objective of current PMD research is the creation of simple systems capable of efficient, long-lived photoinduced charge-separation (PICS). As well as being fundamental to photosynthesis, PICS is the key to the functioning of Grätzel-type photovoltaic cells (see section 6 below). Both organic and metal-based species can behave as electron-accepting or donating quenchers.

The most commonly used organic electron acceptor moieties are the viologens (*N*,*N*′-dialkyl-4,4′-bipyridinium cations) and related species such as *N*-methyl-4,4′-bipyridinium (MeQ$^+$). These have been incorporated into many covalently-linked CQ complexes,[84] including polymeric systems.[84c] Non-covalently assembled CQ systems incorporating viologens are also widespread,[85–89] including species involving cyclodextrins,[86] catenanes[87] and crown ethers.[88] A fascinating example of such an assembly is provided by Ballardini *et al.* who have described a three-component supramolecular system that mimics an electrical extension cable (**19**).[89] This system comprises an RTB unit bearing a pendant dibenzyl-substituted crown ether (A); a wire-type component (B–H^{3+}) composed of a dialkylammonium and a bipyridinium unit; and a dinaphthyl-functionalized crown ether (C). In solution, A binds to B due to interaction between the dialkylammonium moiety and the crown ether, whilst B binds to C through π-π interactions between the bipyridinium and naphthyl units. Both of these interactions



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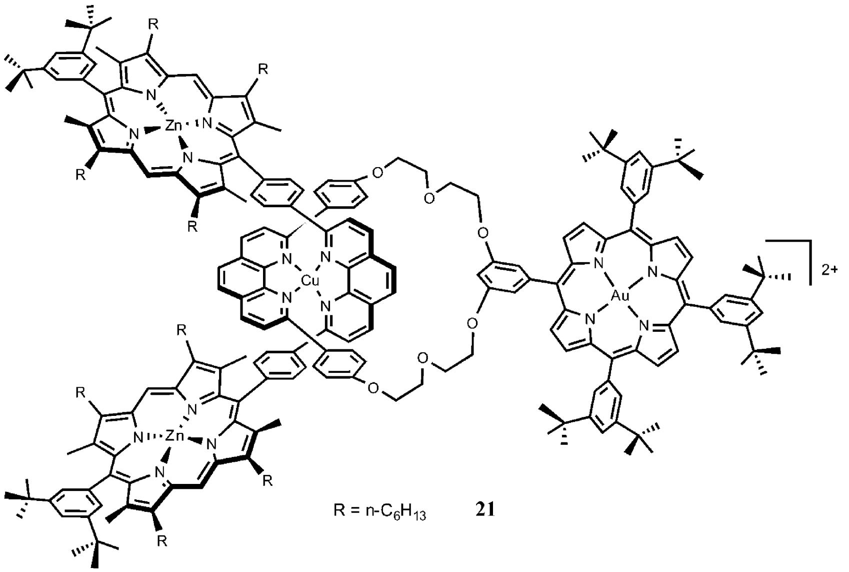
are reversible: deprotonation leads to the dethreading of A from B, and reduction of the bipyridinium unit of B disrupts the interaction between B and C. In the fully assembled system, photoinduced electron-transfer occurs between the RTB moiety and the bipyridinium unit with a rate constant $k = 2.8 \times 10^8\,s^{-1}$.

Anthraquinones have also been widely used as electron acceptors in CQ systems,[90–93] including dendrimeric[91] and polymeric[92] species. A notable report by Ito, Fukuzumi and co-workers describes a ferrocenyl-anthraquinone (Fc-AQ) dyad that exhibits PICS resulting from Fc to AQ electron-transfer.[93] The charge-separated (CS) state has a lifetime of 12 ps, but in the presence of $Y^{III}(OTF)_3$, this lifetime is extended to 83 μs. The authors suggest that strong binding between the CS state and $Y^{III}(OTF)_3$ results in a large solvent reorganization energy barrier (λ) to charge recombination.

Fullerenes have also become popular as components of CQ systems,[94–100] because they are good electron acceptors[95–100] and can also undergo energy-transfer.[98–100] Guldi *et al.* have reported a Ru^{II} porphyrin bearing an axially-coordinated fulleropyrrolidine ligand (RuPorph-C_{60}, **20**).[100] The RuP triplet state that results from photoexcitation of the molecule is quickly deactivated in solution. The quenching mechanism is solvent dependant: in non-polar media such as toluene, triplet energy-transfer is thermodynamically favored. However, in more polar solvents such as benzonitrile or THF, the driving force for RuP to C_{60} electron-transfer is greater than that for energy-transfer, and is similar to λ. Almost activationless RuP to C_{60} electron-transfer occurs, and the subsequent CS state lifetime is long and decreases with increasing concentration. The authors propose that the C_{60} ligand dissociates from RuP in the CS state and that charge recombination requires the reassociation of the RuP-C_{60} complex.

Other well-studied CQ assemblies include mixed-metal multi-porphyrin arrays.[101] Such systems have been shown to exhibit photoinduced energy-transfer[102,103d,e] and PICS.[103] A series of recent reports by Collin, Flamigni, Sauvage and co-workers describes the photophysical behavior of triads PorphH$_2$-Ir-AuPorph and ZnPorph-Ir-AuPorph, consisting of an Ir^{III} bis-tpy complex with a covalently-bound free-base or Zn^{II} porphyrin electron donor unit (PorphH$_2$ or ZnPorph) and Au^{III} porphyrin (AuPorph^{+}) acceptor.[103a-d] Following visible excitation, both triads exhibit PICS. In the triad with the free-base porphyrin in acetonitrile, the CS state (PorphH$_2^{\cdot+}$-Ir-AuPorph$^{\cdot}$) is short-lived (3.5 ns),[103a,c] but with the Zn^{II} porphyrin in toluene, the lifetime of the CS state (ZnPorph$^{\cdot+}$-Ir-AuPorph$^{\cdot}$) is 450 ns.[103b,c] A later study has shown that UV excitation of the Ir^{III} bis-tpy unit of PorphH$_2$-Ir-AuPorph leads to energy-transfer to the porphyrin units, while PICS occurs in ZnPorph-Ir-AuPorph irrespective of which unit is excited.[103d]



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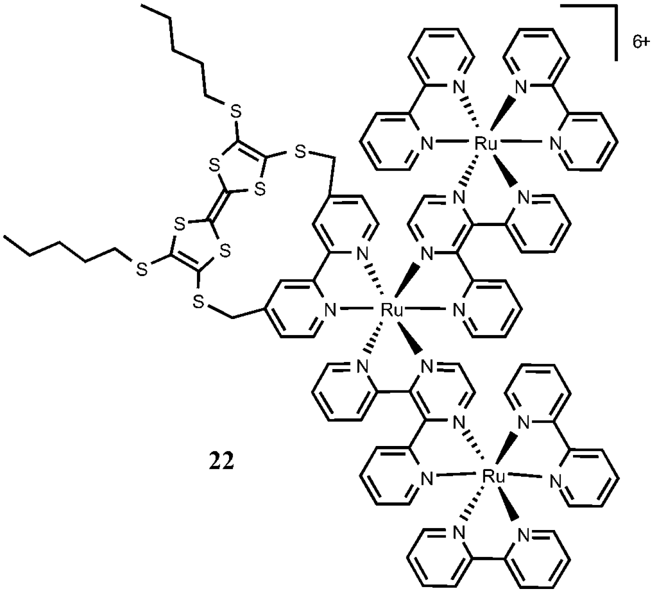
Hammarström, Sauvage and co-workers have studied porphyrin-containing [2]-rotaxanes (**21**) in which two ZnPorphs act as stoppers on the rod and an AuPorph is attached to a macrocycle threaded onto the rod.[103e] Selective excitation of either ZnPorph or AuPorph leads to the formation of CS states, ZnPorph$^{\bullet+}$-AuPorph$^{\bullet}$, which have lifetimes of 10–40 ns. Both rod and macrocycle contain phen units, such that a Cu^{I} or Ag^{I} ion can be coordinated between the ZnPorph and AuPorph units. Such metal coordination enhances the charge-transfer rate following excitation of AuPorph, but has no effect on the kinetics when ZnPorph is excited. The authors propose that the mechanism of PICS depends upon the excited porphyrin, with hole-transfer following excitation of AuPorph and electron-transfer resulting from excitation of ZnPorph. With coordinated Cu^{I}, ^{1}ZnPorph to $\{Cu(phen)_2\}^{+}$ energy-transfer competes with PICS as the quenching mechanism.

In a recent study, Campagna *et al.* have prepared a trinuclear complex which combines energy and electron-transfer (**22**).[104] This molecule consists of a central Ru^{II} polypyridyl complex bearing a tetrathiofulvalene (TTF) electron donor unit and two peripheral Ru^{II} polypyridyl units.



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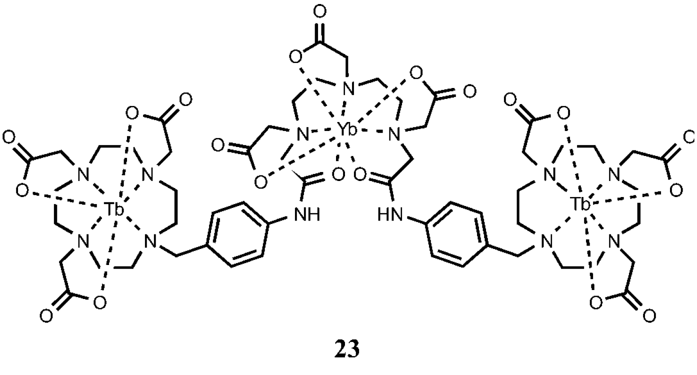
Following light absorption, the central Ru^{II} unit is deactivated by fast energy-transfer to the peripheral ones, with subsequent electron-transfer from the TTF moiety to the peripheral Ru^{II} centers.

Polypyridyl complexes of d-block metal ions, in particular Os^{II}, have been widely used as energy acceptors in CQ assemblies.[105] Very recently, systems have been reported which combine d- and f-block metals, where the d-metal sensitizes Ln emission by energy-transfer. For example, van Veggel and co-workers have prepared *m*-terphenyl complexes of Nd^{III} and Yb^{III} covalently linked to a RTB center ($(Ln_2\text{-}Ru)^{2+}$) or a Fc unit (Ln-Fc).[106] Visible excitation leads to NIR luminescence from the Ln (at 1060 and 1330 nm for Nd^{III} or 975 nm for Yb^{III}). The excitation spectra of $(Ln_2\text{-}Ru)^{2+}$ and Ln-Fc closely match the absorption profiles of the RTB or Fc component, confirming that the d-metal complex is the light-absorbing antenna. In $(Nd_2\text{-}Ru)^{2+}$, the rise-time of the Nd^{III} emission matches the decay-time of the triplet MLCT state of the Ru^{II} chromophore. The energy-transfer rates are low ($k \sim 10^6\,s^{-1}$ for $(Nd_2\text{-}Ru)^{2+}$ and $\leq 10^5\,s^{-1}$ for $(Yb_2\text{-}Ru)^{2+}$), and the authors propose that the difference in rate is due to better energy matching between the Ln^{III} emitting state and the ^{3}MLCT state in $(Nd_2\text{-}Ru)^{2+}$.

Imbert *et al.* have described unusual triple-stranded helicates containing Cr^{III}-Ln^{III} pairs: CrNd and CrYb.[107] These complexes exhibit NIR emission from the Ln^{III} center which is sensitized by energy-transfer from the Cr^{III} excited state. The Ln^{III}-based emission lifetimes are extended in the complex, and match the shortened lifetime of the Cr^{III}-



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based emission. In a further interesting development, Faulkner and Pope have reported the first example of Ln-based NIR emission sensitized by another Ln ion.[108] They describe the preparation of a trinuclear complex (**23**) comprising two Tb^{III} ions, which occupy 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid-type binding sites, and an Yb^{III} ion in a diethylenetriamine pentaacetic acid-derived site. Selective excitation of the Tb^{III} ions at 448 nm results in Yb^{III}-based emission at 980 nm. Since neither the ligand nor the Yb^{III} absorb at 448 nm, the data indicate that Tb^{III} to Yb^{III} energy-transfer occurs.

6. DYE-SENSITIZED PHOTOVOLTAIC CELLS

Perhaps the most important technology to exploit the photoexcitation properties of metal complexes will arise from the development of dye-sensitized photovoltaic cells. Traditionally constructed solar cells rely upon the direct absorption of photons by a semiconducting material. However, the efficiency of such cells is limited because the absorption of visible light requires narrow band-gap semiconductors, which are inherently unstable with respect to photodegradation. In a major breakthrough in 1991, O'Regan and Grätzel reported efficient photoinduced sensitization of a nanoparticulate wide band-gap semiconductor by a trinuclear ruthenium bpy-based dye.[109] Since then, there has been widespread interest in this field, and a number of reviews have been published.[110]

A dye-sensitized photovoltaic cell contains a nanoparticulate film of a wide band-gap semiconducting material such as TiO_2, coated with a monolayer of a sensitizing dye. Absorption of light by the dye results in electron-transfer into the conduction band of the semiconductor. The oxidized dye is then reduced back to its original oxidation state by a species in the electrolyte (usually an organic solvent containing the I^-/I_3^- couple), which is in turn regenerated at a counter electrode (Figure 1).

Grätzel has defined the properties of an ideal sensitizing dye as follows:[110c] (i) absorbs all light at wavelengths below 920 nm; (ii) functionalized with groups such as carboxylate or phosphonate, which can adhere to the oxide surface; (iii) undergoes photoinduced electron-transfer into the semiconductor with a quantum yield of unity; (iv) has an excited-state well matched in energy with the lower limit of the conduction band of the semiconductor; (v) has a redox potential high enough to allow it to be

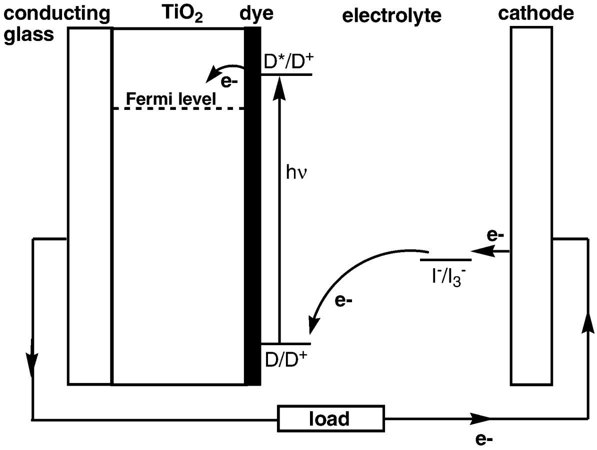
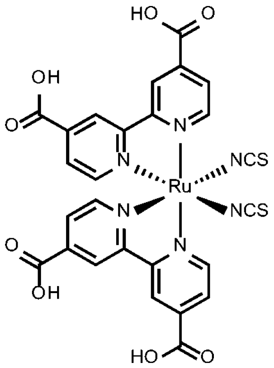


Figure 1. Schematic diagram showing the operation of a dye-sensitized photovoltaic cell.

regenerated by reduction by the redox electrolyte or hole conductor; (vi) stable over about 10^8 turnover cycles.

Probably the most widely studied photosensitizing dye is *cis*-[Ru^{II}(4,4′-dicarboxy-2,2′-bipyridyl)$_2$(NCS)$_2$], known as the N3 dye (**24**).[111] This complex gives an incident photon-to-current conversion efficiency (IPCE) of over 80% between 480 and 600 nm. Photovoltaic cells based on N3 have been the subject of many reports,[112] including time-resolved



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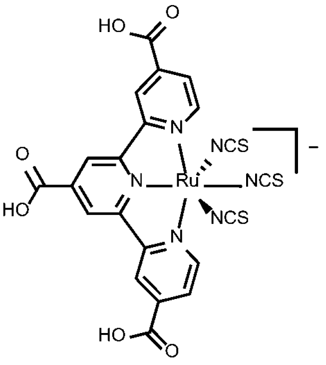

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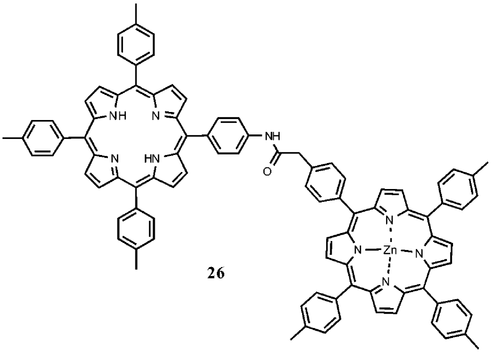
photophysical studies.[112a,d] In a very recent study by Durrant and co-workers, the N3 dye has been incorporated into a flexible photovoltaic cell, which exhibits an overall solar light to electrical energy conversion efficiency of around 5.3%.[112e] A later development of the N3 dye is the complex $[Ru^{II}(tctpy)(NCS)_3]^-$ (tctpy = 4,4′,4″ -tricarboxy-2,2′:6′,″-terpyridyl), known as the black dye (**25**).[113] The absorption spectrum of this complex is red-shifted compared to that of N3, and its photocurrent action spectrum extends over the entire visible region and into the NIR. A further study has explored the effect of the degree of carboxylate protonation on the solar IPCE of the black dye;[114] the monoprotonated dye is the most efficient form, with an overall conversion efficiency of 10.4%.

In a further extension of the above work, Renouard *et al.* have developed dyes of the type *trans*-$[Ru^{II}L(NCS)_2]$, where L is a tetradentate imine ligand.[115] Such dyes are designed to absorb more strongly in the red region of the visible spectrum. Interestingly, Liu and Meyer recently demonstrated that it is possible to sensitize TiO_2 to visible light by using a Ru^{II} dye containing only a single pyridyl ligand.[116] However, solar cells containing this dye are inefficient due to slow iodide oxidation, which allows charge recombination between the dye and the semiconductor.

Whilst Ru^{II}-based dyes are particularly efficient and well-studied photosensitizers, other d-transition metals can also function in this role. Photovoltaic cells sensitized by complexes of Pt^{II},[117] Os^{II},[118] Re^{I}[119] and Cu^{I}[120] have recently been reported. Somewhat suprisingly, in 1998, Ferrere and Greg reported that the non-emissive iron complex, $[Fe^{II}$(2,2′-bipyridyl-4,4′-dicarboxylic acid$)_2(CN)_2]$, can also act as an efficient photosensitizer.[121a] Further studies have investigated the effects of ligand structure[121b] and solvatochromism[121c] on the photosensitizing properties of such dyes. Related work by Meyer and co-workers shows that the complex $[Fe^{II}(bpy)(CN)_4]^{2-}$ sensitizes TiO_2 to visible light *via* two distinct pathways: direct electron transfer from the $(d\pi)^6$ iron center, and indirect transfer from the $(d\pi)^5(\pi^*)^1$ MLCT state.[122] Although Fe^{II} complexes are less efficient photosensitizers than their Ru^{II} analogues, they are nevertheless attractive candidates for solar energy conversion due to the considerably lower cost of iron.

Metalloporphyrins can also act as sensitizers in photovoltaic cells. Wróbel *et al.* have compared the photosensitizing properties of zinc-, magnesium- and lead-containing tetraphenylporphyrin in cells with



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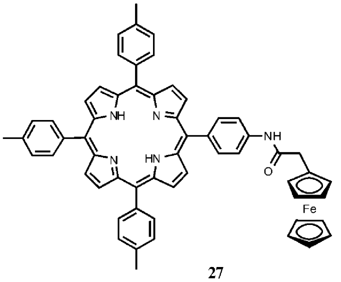

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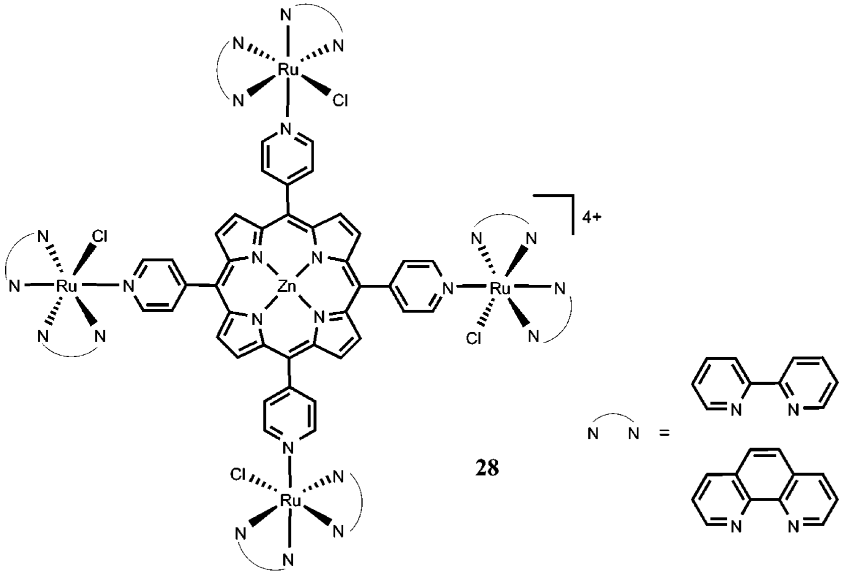
In_2O_3 and gold electrodes.[123] In such systems, photocurrent generation is metal dependent, with the Zn^{II}-porphyrin giving the highest photocurrent, whilst the Pb^{II}-porphyrin is inactive. Durantini and co-workers have prepared dyads in which a free-base porphyrin is linked to a Zn^{II}-porphyrin (**26**) or Fc group (**27**) by an amide bond.[124] SnO_2 electrodes coated with these dyads give IPCEs of about 10%.



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Very recent work by Toma and co-workers has involved the preparation of *meso*-tetrapyridylporphyrin (TpyPorph) coordinated to two or four *cis*-$[Ru^{II}(phen)_2Cl]^+$ units.[125] The Ru_2TpyPorph species photosensitizes TiO_2 with a maximum IPCE of 21%, but negligible photocurrent is observed when using the Ru_4TpyPorph compound. The authors hence infer that an uncoordinated pyridyl moiety is necessary to ensure effective binding of the porphyrin to the semiconductor surface. In a related study, Zn^{II}-tetrapyridylporphyrin was coordinated to four *cis*-$[Ru^{II}(phen)_2Cl]^+$ or *cis*-$[Ru^{II}(bpy)_2Cl]^+$ units (**28**).[126] In contrast to their free-base analogues, the tetra-substituted Zn^{II}-porphyrins give IPCEs of up to 13%, apparently due to interactions between the Zn^{II} ion and the semiconductor surface.

7. ORGANIC LIGHT-EMITTING DIODES

The development of organic light-emitting diodes (OLEDs) is of great importance for modern technologies such as flat-screen displays. Full color displays require efficient emission of pure red, green and blue light, and the preparation of materials with such photophysical characteristics has become a target for synthetic chemists. Light-emitting diodes rely on the phenomenon of electroluminescence (EL), or light emission resulting from the application of an electric field to a material.[127]

Single layer OLEDs (Figure 2a) consist of a layer of an emitting species (such as poly(*para*-phenylenevinylene) or PPV), or a host material doped with an emitting species, sandwiched between two electrodes. Electrons are injected from the cathode (usually a metal such as aluminum) into the LUMO of the material, and holes migrate from the anode (usually a semi-transparent material such as ITO-coated glass) into the HOMO. Where electrons and holes meet, formation of a singlet or triplet exciton leads to photon emission. A drawback in such systems is that the active layer may not transport holes and electrons with equal efficiency.

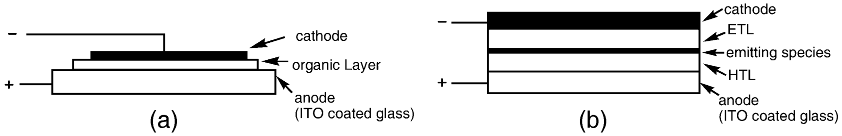
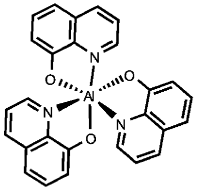


Figure 2. Schematic diagram showing the structures of single layer (a) and multilayer (b) OLEDs.



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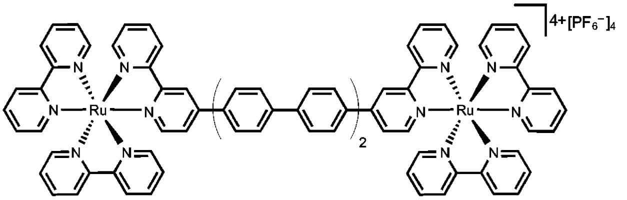

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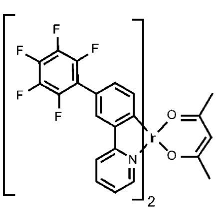
Multilayer OLEDs (Figure 2b) separate the electron and hole-transporting materials into two layers, with the emitting species either held between the electron-transporting layer (ETL) and hole-transporting layer (HTL), or present in either layer.

Devices based on the intensely emissive chelate complex tris(8-hydroxyquinolato)aluminium(III) (Alq_3, **29**) have been extensively studied.[128] The emission wavelength of Alq_3 can be tuned by molecular engineering:[129–131] for example, bis(2-methyl-8-quinolato)hydroxoaluminium(III) has been shown to give efficient, blue-emitting OLEDs.[130] Chen *et al.* have reported yellow and blue emissions from devices based on the complexes tris[5-(methylmalononitrile)-8-hydroxyquinolato]aluminium(III) and tris(2,3-dimethyl-8-hydroxyquinolato)aluminium(III), respectively.[131]

Polypyridyl complexes of Ru^{II}, Os^{II} and Re^{I} have also been exploited in OLEDs, either incorporated into organic polymers[132] and oligomers[133] or doped into the emitting layer of the device.[134] A very exciting report by Welter *et al.* describes an OLED based on PPV doped with a dinuclear Ru^{II} complex salt $[\{Ru\}L–L\{Ru\}][PF_6]_4$ (**30**)[135] ($\{Ru\}$ = cis-$\{Ru(bpy)_2\}^{2+;}$ L–L = 4,4‴-bis(2,2′-bipyridyl)tetra-1,4-phenylene). This device permits reversible switching between green and red emissions due to a difference in the LUMO energies of the complex and the host polymer. Application of a forward bias at the ITO electrode results in hole injection into the HOMOs of both $[\{Ru\}L–L\{Ru\}]^{4+}$ and PPV, but electron injection into the LUMO of the complex cation only. Ruthenium-centred red EL is then observed. However, when a reverse bias is applied, electron-transfer occurs between the reduced $[\{Ru\}L–L\{Ru\}]^{2+}$ and the oxidized $PPV^{\cdot+}$, resulting in green emission from the PPV singlet excited state. Recently, solid-state devices containing spin-cast films of RTB and related compounds have been reported.[136] Gao and Bard have described bright red (660 nm) emission at a turn-on voltage of 2.3 V from a thin film of RTB on ITO-coated glass with a Ga:In cathode.[136b]



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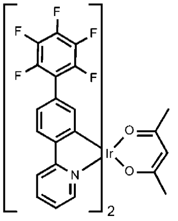

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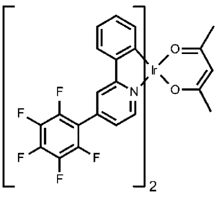

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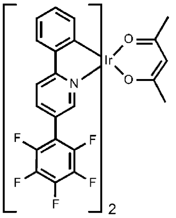

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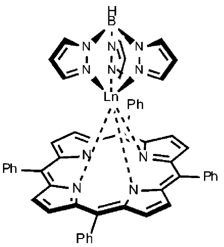
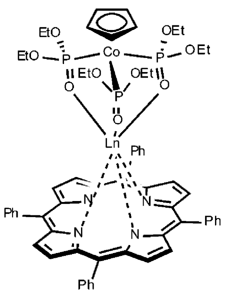
Cyclometallated complexes of Ir^{III} are widely used as emitting species in OLEDs.[137] A recent study by Tsuzuki and co-workers investigated the effect of substituents on the EL wavelengths of OLEDs based on bis(2-phenylpyridinato)(acetylacetonato)iridium(III), lr(ppy)$_2$(acac).[138] Complexes *meta*-PF-Ph (**31**), *para*-PF-Ph (**32**), *meta*-PF-py (**33**) and *para*-PF-py (**34**), bearing pentafluorophenyl (PF) substituents on the phenyl (Ph) or pyridyl (py) ring, were compared with the unsubstituted parent Ir(ppy)$_2$(acac). Multilayered devices containing these complexes doped into 4,4′-di(carbazole-9-yl)biphenyl (CBP) produce emissions varying from green to orange, with wavelengths between 513 nm for devices based on *meta*-PF-Ph and 578 nm with *meta*-PF-py.

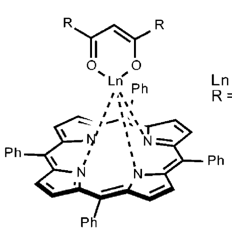
Other d-block metal ions incorporated into EL devices include Co^{III},[139] Zn^{II}[129] and Pt^{II}.[140] OLEDs based on Ln complexes are also widespread due to the well-defined emission properties of such compounds.[141] In particular, the NIR emissions of the later lanthanides have



35



36



37

Ln = Yb, Tm, Er, Ho
R = Me, Ph

potential applications in telecommunications. Schanze and co-workers have studied a series of multilayer OLEDs based on tetraphenylporphyrins, Ln(TPPorph)L, where L is a capping ligand [tris(pyrazolyl)borate (**35**), $[CpCo\{PO(OEt)_2\}_3]^-$ (**36**) or β-diketonate (**37**)].[142] The active layer consists of a spin-coated film of a blue-emitting poly(*para*-phenylene) (PPP-OR11) and Ln(TPPorph)L. These Yb, Ho, Er and Tm-based devices show characteristic Ln-based NIR emissions at 977, 1197, 1570 and 1800 nm, respectively, which are sensitized by energy-transfer from the host polymer.

8. CONCLUSIONS AND OUTLOOK

From a historical perspective, d-transition metal chemistry has always been characterized by its colorful nature and fascinating range of redox properties. The study of f-block complexes is a somewhat less well-developed discipline, but growing apace and often colorful also, owing to the diverse luminescence properties of such compounds. The desire to realize molecular electronic and photonic technologies has given a huge boost to research involving transition metal complexes over the past 15 years or so. Such studies are not only fundamentally interesting and valuable, but are also driven by the firm belief that the exploitation of carefully designed metal complexes will afford exciting advances which may not even be possible using purely organic materials. Although to our knowledge, viable commercial devices based on metal complexes having any of the properties discussed above have yet to appear, it is surely only a matter of time before this is no longer the case. In particular, metal complex-containing dye-sensitized photovoltaic cells and OLEDs are relatively established sciences which have been well-studied at the prototype device stage. The extent to which the various fields discussed reach practically useful maturity (or not) will depend upon various inherent aspects, but also effective communication between synthetic materials-oriented molecular inorganic chemists, physicists and other relevant scientists such as device engineers. Given the rapid progress made over recent years, future prospects for applications of metal complexes in molecular electronic and photonic devices look very bright indeed.

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REFERENCES

1. (a) Ikeda, T., 2003. *J. Mater. Chem.,* **13**, 2037–2057; (b) Tsutsumi, O. and T. Ikeda, 2003. *Current Opinion in Solid State and Materials Science,* **6**, 563–568; (c) Mallia, V. A. and N. Tamaoki, 2004. *Chem. Soc. Rev.,* **33**, 76–84.
2. Gray, G. W. and S. M. Kelly, 1999. *J. Mater. Chem.,* **9**, 2037–2050; (b) Kirsch, P. and M. Bremer, 2000. *Angew. Chem. Int. Ed.,* **39**, 4216–4235.
3. (a) Date, R. W., E. Fernandez Iglesias, K. E. Rowe, J. M. Elliott, and D. W. Bruce, 2003. *Dalton Trans.,* 1914–1931; (b) Serrano, J. L. and R. T. Sierra, 2003. *Coord. Chem. Rev.,* **242**, 73–85; (c) Binnemans, K. and C. Görller-Walrand, 2002. *Chem. Rev.,* **102**, 2303–2345; (d) Gimenez, R., D. P. Lydon, and J. L. Serrano, 2002. *Current Opinion in Solid State & Materials Science,* **6**, 527–535; (e) Donnio, B., 2002. *Current Opinion in Colloid & Interface Science,* **7**, 371–394; (f) Imrie, C., P. Engelbrecht, C. Loubser, C. W. McCleland., 2001. *Appl. Organomet. Chem.,* **15**, 1–15; (g) Chisholm, M. H., 2000. *Acc. Chem. Res.,* **33**, 53–61.
4. Binnemans, K. and K. Lodewyckx, 2001. *Angew. Chem. Int. Ed.,* **40**, 242–244.
5. Galyametdinov, Y. G., L. V. Malykhina, W. Haase, K. Driesen, and K. Binnemans, 2002. *Liquid Crystals,* **29**, 1581–1584.
6. Yu, S. C., S. Hou, and W. K. Chan, 2000. *Macromolecules,* **33**, 3259–3273.
7. Monobe, H., Y. Miyagawa, S. Mima, T. Sugino, K. Uchida, and Y. Shimizu. 2001. *Thin Solid Films,* **393**, 217–224.
8. Qi, M.-H. and G.-F. Liu, 2003. *J. Mater. Chem.,* **13**, 2479–2484.
9. Fanizzi, F. P., V. Alicino, C. Cardellicchio, P. Tortorella, and J. P. Rourke, 2000. *Chem. Commun.,* 673–674.
10. Ziessel, R., 2001. *Coord. Chem. Rev.,* **216–217**, 195–223.
11. El-ghayoury, A., L. Douce, A. Skoulios, and R. Ziessel, 1998. *Angew. Chem. Int. Ed.,* **37**, 2205–2208.
12. Ziessel, R., L. Douce, A. El-ghayoury, A. Harriman, and A. Skoulios, 2000. *Angew. Chem. Int. Ed.,* **39**, 1489–1493.
13. Douce, L., T. H. Diep, R. Ziessel, A. Skoulios, and M. Césario, 2003. *J. Mater. Chem.,* **13**, 1533–1539.
14. Barberá, J., E. Cavero, M. Lehmann, J.-L. Serrano, T. Sierra, and J. T. Vázquez, 2003. *J. Am. Chem. Soc.,* **125**, 4527–4533.
15. Nalwa, H. S. and S. Miyata (Eds.), 1997. Nonlinear Optics of Organic Molecules and Polymers, CRC Press, Boca Raton, FL.
16. Selected recent reviews: (a) Di Bella, S., 2001. *Chem. Soc. Rev.,* **30**, 355–366; (b) Coe, B. J., in: McCleverty, J. A. and Meyer, T. J., (Eds.), 2004. *Comprehensive Coordination Chemistry II.*, vol. **9**, pp. 621–687, Elsevier-Pergamoni, Oxford, U.K.

17. (a) Farrell, T., T. Meyer-Friedrichsen, M. Malessa, D. Haase, W. Saak, I. Asselberghs, K. Wostyn, K. Clays, A. Persoons, J. Heck, and A. R. Manning, 2001. *J. Chem. Soc., Dalton Trans.,*. 29–36; (b) Farrell, T., A. R. Manning, G. Mitchell, J. Heck, T. Meyer–Friedrichsen, M. Malessa, C. Wittenburg, M. H. Prosenc, D. Cunningham, and P. McArdle, 2002. *Eur. J. Inorg. Chem.,* 1677–1686.
18. Chiffre, J., F. Averseng, G. G. A. Balavoine, J.-C. Daran, G. Iftime, P. G. Lacroix, E. Manoury, and K. Nakatani, 2001. *Eur. J. Inorg. Chem.,* 2221–2226.
19. Li, G., Y.-L. Song, H.-W. Hou, L. Li, Y.-T. Fan, Y. Zhu, X.-G. Meng, and L.-W. Mi, 2003. *Inorg. Chem.,* **42**, 913–920.
20. Venkatraman, S., R. Kumar, J. Sankar, T. K. Chandrashekar, K. Sendhil, C. Vijayan, A. Kelling, and M. O. Senge, 2004. *Chem. Eur. J.,* **10**, 1423–1432.
21. (a) Coe, B. J., S. Houbrechts, I. Asselberghs, and A. Persoons, 1999. *Angew. Chem. Int. Ed.,* **38**, 366–369; (b) Coe, B. J., 1999. *Chem. Eur. J.,* **5**, 2464–2471.
22. Selected examples: (a) Weyland, T., I. Ledoux, S. Brasselet, J. Zyss, and C. Lapinte, 2000. *Organometallics,* **19**, 5235–5237; (b) Malaun, M., R. Kowallick, A. M. McDonagh, M. Marcaccio, R. L. Paul, I. Asselberghs, K. Clays, A. Persoons, B. Bildstein, C. Fiorini, J.-M. Nunzi, M. D. Ward, and J. A. McCleverty, 2001. *J. Chem. Soc., Dalton Trans.,* 3025–3038; (c) Powell, C. E., M. P. Cifuentes, J. P. Morrall, R. Stranger, M. G. Humphrey, M. Samoc, B. Luther-Davies, and G. A. Heath, 2003. *J. Am. Chem. Soc.,* **125**, 602–610; (d) Asselberghs, I., K. Clays, A. Persoons, A. M. McDonagh, M. D. Ward, and J. A. McCleverty, 2003. *Chem. Phys. Lett.,* **368**, 408–411.
23. (a) Coe, B. J., L. A. Jones, J. A. Harris, B. S. Brunschwig, I. Asselberghs, K. Clays, and A. Persoons, 2003. *J. Am. Chem. Soc.,* **125**, 862–863; (b) Coe, B. J., L. A. Jones, J. A. Harris, B. S. Brunschwig, I. Asselberghs, K. Clays, A. Persoons, J. Garín, and J. Orduna, 2004. *J. Am. Chem. Soc.,* **126**, 3880–3891.
24. Tessore, F., D. Roberto, R. Ugo, P. Mussini, S. Quici, I. Ledoux-Rak, and J. Zyss, 2003. *Angew. Chem. Int. Ed.,* **42**, 456–459.
25. Evans, O. R. and W. Lin, 2002. *Acc. Chem. Res.,* **35**, 511–522.
26. Meng, X.-G., Y.-L. Song, H.-W. Hou, Y.-T. Fan, G. Li, and Y. Zhu, 2003. *Inorg. Chem.,* **42**, 1306–1315; Niu, Y.-Y., Y.-L. Song, J. Wu, H.-W. Hou, Y. Zhu, and X. Wang, 2004. *Inorg. Chem. Commun.,* **7**, 471–474.
27. Han, L., M.-C. Hong, R.-H. Wang, J.-H. Luo, Z.-Z. Lin, and D.-Q. Yuan, 2003. *Chem. Commun.,* 2580–2581.
28. (a) Le Bouder, T., O. Maury, H. Le Bozec, I. Ledoux, and J. Zyss, 2001. *Chem. Commun.,* 2430–2431; (b) Le Bozec, H., T. Le Bouder, O. Maury, A. Bondon, I. Ledoux, S. Deveau, and J. Zyss, 2001. *Adv. Mater.,* **13**,

1677–1681; (c) Le Bouder, T., O. Maury, O. Bondon, K. Costuas, E. Amouyal, I. Ledoux, J. Zyss, and H. Le Bozec, 2003. *J. Am. Chem. Soc.,* **125**, 12284–12299.

29. Sénéchal, K., O. Maury, H. Le Bozec, I. Ledoux, and J. Zyss, 2002. *J. Am. Chem. Soc.,* **124**, 4560–4561.
30. Fave, C., M. Hissler, K. Sénéchal, I. Ledoux, J. Zyss, and R. Réau, 2002. *Chem. Commun.,* 1674–1675.
31. Kar, S., T. A. Miller, S. Chakraborty, B. Sarkar, B. Pradhan, R. K. Sinha, T. Kundu, M. D. Ward, and G. K. Lahiri, 2003. *Dalton Trans.,* 2591–2596.
32. Roberto, D., F. Tessore, R. Ugo, S. Bruni, A. Manfredi, and S. Quici, 2002. *Chem. Commun.,* 846–847.
33. Konstantaki, M., E. Koudoumas, S. Couris, P. Laine, E. Amouyal, and S. Leach, 2001. *J. Phys. Chem., B* **105**, 10797–10804.
34. Selected recent examples: (a) Hurst, S. K., M. G. Humphrey, T. Isoshima, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, and B. Luther-Davies, 2002. *Organometallics,* **21**, 2024–2026; (b) Hurst, S. K., M. G. Humphrey, J. P. Morrall, M. P. Cifuentes, M. Samoc, B. Luther-Davies, G. A. Heath, and A. C. Willis, 2003. *J. Organomet. Chem.,* **670**, 56–65; (c) Powell, C. E., M. P. Cifuentes, A. M. McDonagh, S. K. Hurst, N. T. Lucas, C. D. Delfs, R. Stranger, M. G. Humphrey, S. Houbrechts, I. Asselberghs, A. Persoons, and D. C. R. Hockless, 2003. *Inorg. Chim. Acta,* **352**, 9–18.
35. Garcia, M. H., M. P. Robalo, A. R. Dias, M. T. Duarte, W. Wenseleers, G. Aerts, E. Goovaerts, M. P. Cifuentes, S. Hurst, M. G. Humphrey, M. Samoc, and B. Luther-Davies, 2002. *Organometallics,* **21**, 2107–2118.
36. Ogawa, K., T.-Q. Zhang, K. Yoshihara, and Y. Kobuke, 2002. *J. Am. Chem. Soc.,* **124**, 22–23.
37. Screen, T. E. O., J. R. G. Thorne, R. G. Denning, D. G. Bucknall, and H. L. Anderson, 2002. *J. Am. Chem. Soc.,* **124**, 9712–9713.
38. Uyeda, H. T., Y.-X. Zhao, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, and M. J. Therien, 2002. *J. Am. Chem. Soc.,* **124**, 13806–13813.
39. Yang, G. Y., S. G. Ang, L. L. Chng, Y. W. Lee, E. W.-P. Lau, K. S. Lai, and H. G. Ang, 2003. *Chem. Eur. J.,* **9**, 900–904.
40. Chen, Y., L. R. Subramanian, M. Fujitsuka, O. Ito, S. O'Flaherty, W. J. Blau, T. Schneider, D. Dini, and M. Hanack, 2002. *Chem. Eur. J.,* **8**, 4248–4254.
41. O'Flaherty, S. M., S. V. Hold, M. J. Cook, T. Torres, Y. Chen, M. Hanack, and W. J. Blau, 2003. *Adv. Mater.,* **15**, 19–32.
42. Di Bella, S. and I. Fragalà, 2003. *Eur. J. Inorg. Chem.,* **7**, 2606–2611.
43. Cariati, F., U. Caruso, R. Centore, W. Marcolli, A. De Maria, B. Panunzi, A. Roviello, and A. Tuzi, 2002. *Inorg. Chem.,* **41**, 6597–6603.
44. Zhang, G.-H., D. Xu, M.-K. Lu, D.-R. Yuan, X.-Q. Wang, F.-Q. Meng, S.-Y. Guo, Q. Ren, and M.-H. Jiang, 2001. *Opt. Laser Technol.*, **33**, 121–124.

45. Tan, W.-L., W. Ji, J.-L. Zuo, J.-F. Bai, X.-Z. You, J.-H. Lim, S. Yang, D. J. Hagan, and E. W. Van Stryland, 2000. *Appl. Phys. B*, **70**, 809–812.
46. Dai, J., G.-Q. Bian, X. Wang, Q.-F. Xu, M.-Y. Zhou, M. Munakata, M. Maekawa, M.-H. Tong, Z.-R. Sun, and H.-P. Zeng, 2000. *J. Am. Chem. Soc.*, **122**, 11007–11008.
47. Bigoli, F., C.-T. Chen, W.-C. Wu, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, L. Pilia, G. Pintus, A. Serpe, and E. F. Trogu, 2001. *Chem. Commun.*, 2246–2247.
48. Romaniello, P. and F. Lelj, 2003. *Chem. Phys. Lett.*, **372**, 51–58.
49. Zhang, C., Y.-L. Song, X. Wang, F. E. Kühn, Y.-X. Wang, Y. Xue, and X.-Q. Xin, 2003. *J. Mater. Chem.*, **13**, 571–579.
50. Chen, X.-H., K.-C. Wu, J. G. Snijders, and C.-S. Lin, 2003. *Inorg. Chem.*, **42**, 532–540.
51. Zhang, C., Y.-L. Song, F. E. Kühn, Y.-X. Wang, X.-Q. Xin, and W. A. Herrmann, 2002. *Adv. Mater.*, **14**, 818–822.
52. Zhang, Q.-F., W.-H. Leung, X.-Q. Xin, and H.-K. Fun, 2000. *Inorg. Chem.*, **39**, 417–426.
53. Zhang, H., D. E. Zelmon, L. Deng, H.-K. Liu, and B. K. Teo, 2001. *J. Am. Chem. Soc.*, **123**, 11300–11301.
54. Shi, J.-M., W. Xu, Q.-Y. Liu, F.-L. Liu, Z.-L. Huang, H. Lei, W.-T. Yu, and Q. Fang, 2002. *Chem. Commun.*, 756–757.
55. Xie, Y.-R., H. Zhao, X.-S. Wang, Z.-R. Qu, R.-G. Xiong, X. Xue, Z.-L. Xue, and X.-Z. You, 2003. *Eur. J. Inorg. Chem.*, 3712–3715.
56. Hou, H.-W., Y.-L. Wei, Y.-L. Song, Y.-T. Fan, and Y. Zhu, 2004. *Inorg. Chem.*, **43**, 1323–1327.
57. Selected recent examples: (a) Harriman, A., and R. Ziessel, 1998. *Coord. Chem. Rev.*, **171**, 331–339; (b) Jiang, B., S. W. Yang, S. L. Bailey, L. G. Hermans, R. A. Niver, M. A. Bolcar, and W. E. Jones, Jr., 1998. *Coord. Chem. Rev.*, **171**, 365–386; (c) Paul, F. and C. Lapinte, 1998. *Coord. Chem. Rev.*, **171**, 431–509; (d) Ziessel, R., M. Hissler, A. El-ghayoury, and A. Harriman, 1998. *Coord. Chem. Rev.*, 178–**180**, 1251–1298; (e) Barigelletti, F. and L. Flamigni, 2000. *Chem. Soc. Rev.*, **29**, 1–12; (f) Bera, J. K. and K. R. Dunbar, 2002. *Angew. Chem. Int. Ed.*, **41**, 4453–4457; (g) Robertson, N. and C. A. McGowan, 2003. *Chem. Soc. Rev.*, **32**, 96–103.
58. Zhang, Y., C. B. Murphy, and W. E. Jones, Jr., 2002. *Macromolecules*, **35**, 630–636.
59. Aich, P., S. L. Labivik, L. W. Tari, L. J. T. Delbaere, W. J. Roesler, K. J. Falk, R. P. Steer, and J. S. Lee, 1999. *J. Mol. Biol.*, **294**, 477–485.
60. Recent reviews: (a) Bruce, M. I., 1997. *Coord. Chem. Rev.*, **166**, 91–119; (b) Long, N. J. and C. K. Williams, 2003. *Angew. Chem. Int. Ed.*, **42**, 2586–2617.
61. Dembinski, R., T. Bartik, B. Bartik, M. Jaeger, and J. A. Gladysz, 2000. *J. Am. Chem. Soc.*, **122**, 810–822.

62. (a) Mohr, W., J. Stahl, F. Hampel, and J. A. Gladysz, 2001. *Inorg. Chem.*, **40**, 3263–3264; (b) Mohr, W., J. Stahl, F. Hampel, and J. A. Gladysz, 2003. *Chem. Eur. J.*, **9**, 3324–3340.
63. Yam, V. W.-W., K. M.-C. Wong, and N.-Y. Zhu, 2003. *Angew. Chem. Int. Ed.*, **42**, 1400–1403.
64. Jiao, H.-J., K. Costuas, J. A. Gladysz, J.-F. Halet, M. Guillemot, L. Toupet, F. Paul, and C. Lapinte, 2003. *J. Am. Chem. Soc.*, **125**, 9511–9522.
65. Le Stang, S., F. Paul, and C. Lapinte, 2000. *Organometallics*, **19**, 1035–1043.
66. Xu, D., J. Z. Zhang, and B. Hong, 2001. *J. Phys. Chem. A.*, **105**, 7579–7988.
67. Shiotsuka, M., Y. Yamamoto, S. Okuno, M. Kitou, K. Nozaki, and S. Onaka, 2002. *Chem. Commun.*, 590–591.
68. (a) Xu, G. and T. Ren, 2001. *Inorg. Chem.*, **40**, 2925–2927; (b) Xu, G.-L., G. Zou, Y.-H. Ni, M. C. DeRosa, R. J. Crutchley, and T. Ren, 2003. *J. Am. Chem. Soc.*, **125**, 10057–10065; (c) Xu, G.-L., M. C. DeRosa, R. J. Crutchley, and T. Ren, 2004. *J. Am. Chem. Soc.*, **126**, 3728–3729.
69. Wong, K. T., J.-M. Lehn, S.-M. Peng, and G.-H. Lee, 2000. *Chem. Commun.*, 2259–2260.
70. Jiang, F., G. P. A. Yap, and R. K. Pomeroy, 2002. *Organometallics*, **21**, 773–776.
71. Tejel, C., M. A. Ciriano, B. E. Villarroya, J. A. López, F. J. Lahoz, and L. A. Oro, 2003. *Angew. Chem. Int. Ed.*, **42**, 530–532.
72. Murahashi, T., E. Mochizuki, Y. Kai, and H. Kurosawa, 1999. *J. Am. Chem. Soc.*, **121**, 10660–10661.
73. Murahashi, T., T. Nagai, T. Okuno, T. Matsutani, and H. Kurosawa, 2000. *Chem. Commun.*, 1689–1690.
74. Fabrizzi, L., M. Licchelli, and P. Pallavicini, 1999. *Acc. Chem. Res.*, **32**, 846–853.
75. Fabian, J., H. Nakazumi, and M. Matsuoka, 1992. *Chem. Rev.*, **92**, 1197–1226.
76. Selected recent examples: (a) Barthram, A. M., R. L. Cleary, R. Kowallick, and M. D. Ward, 1998. *Chem. Commun.*, 2695–2696; (b) Barthram, A. M. and M. D. Ward, 2000. *New. J. Chem.*, **24**, 501–504; (c) Bayly, S. R., E. R. Humphrey, H. De Chair, C. G. Paredes, Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, F. Totti, D. Gatteschi, S. Courric, B. R. Steele, and C. G. Screttas, 2001. *J. Chem. Soc., Dalton. Trans.*, 1401–1414; (d) McDonagh, A., M. D. Ward, and J. A. McCleverty, 2001. *New. J. Chem.*, **25**, 1236–1243.; (e) García-Cañadas, J., A. P. Meacham, L. M. Peter, and M. D. Ward, 2003. *Angew. Chem. Int. Ed.*, **42**, 3011–3014.
77. McDonagh, A. M., S. R. Bayly, D. J. Riley, M. D. Ward, J. A. McCleverty, M. A. Cowin, C. N. Morgan, R. Varrazza, R. V. Penty, and I. H. White, 2000. *Chem. Mater.*, **12**, 2523–2524.

78. Kern, J.-M., J.-P. Sauvage, G. Bidan, and B. Divisia-Blohorn, 2003. *J. Polymer. Science, A: Polymer Chemistry*, **41**, 3470–3477.
79. Weber, N., C. Hamann, J.-M. Kern, and J.-P. Sauvage, 2003. *Inorg. Chem.*, **42**, 6780–6792.
80. Soto, E., J. C. MacDonald, C. G. F. Cooper, and W. G. McGimpsey, 2003. *J. Am. Chem. Soc.*, **125**, 2838–2839.
81. Cooper, C. G. F., J. C. MacDonald, E. Soto, and W. G. McGimpsey, 2004. *J. Am. Chem. Soc.*, **126**, 1032–1033.
82. (a) Balzani, V. and F. Scandola, 1991. *Supramolecular Photochemistry.* Ellis Horwood, Chichester; (b) Liddell, P. A., G. Kodis, J. Andréasson, L. de la Garza, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore, A. L. Moore, and D. Gust, 2004. *J. Am. Chem. Soc.*, **126**, 4803–4811 and references therein.
83. Selected recent examples: (a) Flamigni, L., F. Barigelletti, N. Armaroli, J.-P. Collin, I. M. Dixon, J.-P. Sauvage, and J. A. G. Williams, 1999. *Coord. Chem. Rev.*, 190–**192**, 671–682; (b) Kaschak, D. M., S. A. Johnson, C. C. Waraksa, J. Pogue, and T. E. Mallouk, 1999. *Coord. Chem. Rev.*, **185–186**, 403–416; (c) Vlcek Jr., A. 2000. *Coord. Chem. Rev.*, **200–202**, 933–977; (d) Barigelletti, F. and L. Flamigni, 2000. *Chem. Soc. Rev.*, **29**, 1–12; (e) Ward, M. D. and F. Barigelletti, 2001. *Coord. Chem. Rev.*, **216**, 127–154; (f) Prodi, A., M. T. Indelli, C. J. Kleverlaan, E. Alessio, and F. Scandola, 2002. *Coord. Chem. Rev.*, **229**, 51–58.
84. Selected recent examples: (a) Ruthkosky, M., C. A. Kelly, M. C. Zaros, and G. J. Meyer, 1997. *J. Am. Chem. Soc.*, **119**, 12004–12005; (b) Scaltrito, D. V., C. A. Kelly, M. Ruthkosky, M. C. Zaros, and G. J. Meyer, 2000. *Inorg. Chem.*, **39**, 3765–3766; (c) Sykora, M., K. A. Maxwell, J. M. DeSimone, and T. J. Meyer, 2000. *Proc. Nat. Acad. Sci. USA*, **97**, 7687–7691.
85. Dürr, H. and Bossmann, S. 2001. *Acc. Chem. Res.*, **34**, 905–917.
86. Nelissen, H. F. M., M. Kercher, L. De Cola, M. C. Feiters, and R. J. M. Nolte, 2002. *Chem. Eur. J.*, **8**, 5407–5414.
87. Flamigni, L., A. M. Talarico, S. Serroni, F. Puntoriero, M. J. Gunter, M. R. Johnston, and T. P. Jeynes, 2003. *Chem. Eur. J.*, **9**, 2649–2659.
88. Schild, V., D. van Loyen, H. Dürr, H. Bouas-Laurent, C. Turro, M. Wörner, M. Raj Pokhrel, and S. H. Bossmann, 2002. *J. Phys. Chem. A*, **106**, 9149–9158.
89. Ballardini, R., V. Balzani, M. Clemente-León, A. Credi, M. T. Gandolfi, E. Ishow, J. Perkins, J. F. Stoddart, H.-R. Tseng, and S. Wenger, 2002. *J. Am. Chem. Soc.*, **124**, 12786–12795.
90. Selected recent examples: (a) Frank, R., G. Greiner, and H. Rau, 1999. *Phys. Chem. Chem. Phys.*, **103**, 7139–3490; (b) Frank, R. and H. Rau, 2001. *Helv. Chim. Acta.*, **84**, 3837–3848; (c) Ruiz, G. T., M. P. Juliarena, R. O. Lezna, E. Wolcan, M. R. Feliz, and G. Ferraudi, 2002. *Helv. Chim. Acta*, **85**, 1261–1275.

91. (a) Rajesh, C. S., G. J. Capitosti, S. J. Cramer, and D. A. Modarelli, 2001. *J. Phys. Chem. B*, **105**, 10175–10188; (b) Capitosti, G. J., S. J. Cramer, C. S. Rajesh, and D. A. Modarelli, 2001. *Org. Lett.*, **3**, 1645–1648.
92. Catellani, M., S. Luzzati, N.-O. Lupsac, R. Mendichi, R. Consonni, F. Giacalone, J. L. Segura, and N. Martin, 2004. *Thin Solid Films*, **451–452**, 2–6.
93. Okamoto, K., Y. Araki, O. Ito, and S. Fukuzumi, 2004. *J. Am. Chem. Soc.*, **126**, 56–57.
94. Guldi, D. M., 2000. *Chem. Commun.*, 321–327.
95. Loi, M. A., P. Denk, H. Hoppe, H. Neugebauer, C. Winder, D. Meissner, C. Brabec, N. S. Sariciftci, A. Gouloumis, P. Vázquez, and T. Torres, 2003. *J. Mater. Chem.*, **13**, 700–704.
96. Rio, Y., G. Enderlin, C. Bourgogne, J.-F. Nierengarten, J.-P. Gisselbrecht, M. Gross, G. Accorsi, and N. Armaroli, 2003. *Inorg. Chem.*, **42**, 8783–8793.
97. Li, K., D. I. Schuster, D. M. Guldi, M. Á. Herranz, and L. Echegoyen, 2004. *J. Am. Chem. Soc.*, **126**, 3388–3389.
98. Bonifazi, D., M. Scholl, F. Soong, L. Echegoyen, G. Accorsi, N. Armaroli, and F. Diederich, 2003. *Angew. Chem. Int. Ed.*, **42**, 4966–4970.
99. Bell, D. M., K. P. Ghiggino, K. A. Jolliffe, M. G. Ranasinghe, S. J. Langford, M. J. Sheppard, and M. N. Paddon-Row, 2002. *J. Phys. Chem.*, **106**, 10079–10088.
100. Guldi, D. M., T. Da Ros, P. Braiuca, and M. Prato, 2003. *Photochem. Photobiol. Sci.*, **2**, 1067–1073.
101. Choi, M.-S., T. Yamazaki, I. Yamazaki, and T. Aida, 2004. *Angew. Chem. Int. Ed.*, **43**, 150–158.
102. Selected recent examples: (a) Sazanovich, I. V., A. Balakumar, K. Muthukumaran, E. Hindin, C. Kirmaier, J. R. Diers, J. S. Lindsey, D. F. Bocain, and D. Holten, 2003. *Inorg. Chem.*, **42**, 6616–6628; (b) Yu, L., K. Muthukumaran, I. V. Sazanovich, C. Kirmaier, E. Hindin, J. R. Diers, D. F. Bocain, D. Holten, and J. S. Lindsey, 2003. *Inorg. Chem.*, **42**, 6629–6647.
103. Selected recent examples: (a) Dixon, I. M., J.-P. Collin, J.-P. Sauvage, F. Barigelletti, and L. Flamigni, 2000. *Angew. Chem. Int. Ed.*, **39**, 1292–1295; (b) Flamigni, L., I. M. Dixon, J.-P. Collin, and J.-P. Sauvage, *Chem. Commun.*, **2000**, 2479–2480; (c) Dixon, I. M., J.-P. Collin, J.-P. Sauvage, and L. Flamigni, 2001. *Inorg. Chem.*, **40**, 5507–5517; (d) Flamigni, L., G. Marconi, I. M. Dixon, J.-P. Collin, and J.-P. Sauvage, 2002. *J. Phys. Chem. B*, **106**, 6663–6671; (e) Andersson, M., M. Linke, J.-C. Chambron, J. Davidsson, V. Heitz, L. Hammarström, and J.-P. Sauvage, 2002. *J. Am. Chem. Soc.* **124**, 4347–4362; (f) Fukuzumi, S., K. E. W. Ohkubo, Z. Ou, J. Shao, K. M. Kadish, J. A. Hutchinson, K. P. Ghiggino, P. J. Sintic, and M. J. Crossley, 2003. *J. Am. Chem. Soc.*, **125**, 14984–14985.

104. Campagna, S., S. Serroni, F. Puntoriero, F. Loiseau, L. De Cola, C. J. Kleverlaan, J. Becher, A. Ploug Sørensen, P. Hascoat, and N. Thorup, 2002. *Chem. Eur. J.*, **8**, 4461–4469.

105. Selected recent examples: (a) El-ghayoury, A., A. Harriman, and R. Ziessel, 2000. *J. Phys. Chem. A*, **104**, 7906–7915; (b) Fleming, C. N., K. A. Maxwell, J. M. DeSimone, T. J. Meyer, and J. M. Papanikolas, 2001. *J. Am. Chem. Soc.*, **123**, 10336–10347; (c) Argazzi, R., E. Bertolasi, C. Chiorboli, C. A. Bignozzi, M. K. Itokazu, and N. I. Murakami Iha, 2001. *Inorg. Chem.*, **40**, 6885–6891; (d) Hurley, D. J. and Y. Tor, 2002. *J. Am. Chem. Soc.*, **124**, 13231–13241.

106. Klink, S. I., K. Keizer, and van F. C. J. M. Veggel, 2000. *Angew. Chem. Int. Ed.*, **39**, 4319–4321.

107. Imbert, D., M. Cantuel, J.-C. G. Bünzli, G. Bernardinelli, and G. Piguet, 2003. *J. Am. Chem. Soc.*, **125**, 15698–15699.

108. Faulkner, S. and S. J. A. Pope, 2003. *J. Am. Chem. Soc.*, **125**, 10526–10527.

109. O'Regan, B. and M. Grätzel, 1991. *Nature* **335**, 737–740.

110. Selected recent reviews: (a) Bignozzi, C. A., R. Argazzi, and C. J. Kleverlaan, 2000. *Chem. Soc. Rev.*, **29**, 87–96; (b) Grätzel, M. 2001. *Nature*, **414**, 338–344; (c) Grätzel, M. 2003. *J. Photochem. Photobiol. C: Photochem. Rev.*, **4**, 145–153; (d) Nazeeruddin, M. K. and M. Grätzel, in: McCleverty, J. A. and T. J. Meyer, (Eds.), 2004. *Comprehensive Coordination Chemistry II.,* vol. **9**. pp. 719–758, Elsevier-Pergamoni, Oxford, U.K.

111. Nazeeruddin, M. K., A. Kay, I. Rodicio, R. Humphrey-Baker, E. Müller, P. Liska, M. Vlachopoulos, and M. Grätzel, 1993. *J. Am. Chem. Soc.*, **115**, 6382–6390.

112. Selected recent examples: (a) Bach, U., Y. Tachibana, J.-E. Moser, S. A. Haque, J. R. Durrant, M. Grätzel, and D. R. Klug, 1999. *J. Am. Chem. Soc.*, **121**, 7445–7446; (b) Nogueira, A. F., M.-A. De Paoli, I. Montanari, R. Monkhouse, J. Nelson, and J. R. Durrant, 2001. *J. Phys. Chem. B*, **105**, 7517–7524; (c) Benko, G., J. Kallioinen, E. I. Korppi-Tommola, A. P. Yartsev, and V. Sundström, 2002. *J. Am. Chem. Soc.*, **124**, 489–493; (d) Shoute, L. C. T. and G. R. Loppnow, 2003. *J. Am. Chem. Soc.*, **125**, 15636–15646; (e) Haque, S. A., E. Palomares, H. M. Upadhyaya, L. Otley, R. J. Potter, A. B. Holmes, and J. R. Durrant, 2003. *Chem. Commun.*, 3008–3009.

113. Nazeeruddin, M. K., P. Péchy, and M. Grätzel, 1997. *Chem. Commun.*, 1705–1706.

114. Nazeeruddin, M. K., P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphrey-Baker, P. Conte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, and M. Grätzel, 2001. *J. Am. Chem. Soc.*, **123**, 1613–1634.

115. Renouard, T., R.-A. Fallahpour, M. K. Nazeeruddin, R. Humphry-Baker, S. I. Gorelsky, A. B. P. Lever, and M. Grätzel, 2002. *Inorg. Chem.*, **41**, 367–378.
116. Liu, F. and G. Meyer, 2003. *Inorg. Chem.*, **42**, 7351–7353.
117. Selected recent examples: (a) Islam, A., H. Sugihara, K. Hara, L. Pratap-Singh, R. Katoh, M. Yanagida, Y. Takahashi, S. Murata, and H. Arakawa, 2000. *New J. Chem.*, **6**, 343–345; (b) Islam, A., H. Sugihara, K. Hara, L. Pratap-Singh, R. Katoh, M. Yanagida, Y. Takahashi, S. Murata, H. Arakawa, and G. Fujihashi, 2001. *Inorg. Chem.*, **40**, 5371–5380; (c) Geary, E. A., N. Hirata, J. Clifford, J. R. Durrant, S. Parsons, A. Dawson, L. J. Yellowlees, and N. Robertson, 2003. *Dalton Trans.*, 3757–3762.
118. Selected recent examples: (a) Sauvé, G., M. E. Cass, G. Coia, S. J. Doig, I. Lauerman, K. E. Pomykal, and N. S. Lewis, 2000. *J. Phys. Chem. B*, **104**, 6821–6836; (b) Lees, A. C., C. J. Kleverlaan, C. A. Bignozzi, and J. G. Vos, 2001. *Inorg. Chem.*, **40**, 5343–5349.
119. Selected recent examples: (a) Asbury, J., E. Hao, Y. Wang, and T. Lian, 2000. *J. Phys. Chem. B*, **104**, 11957–11964; (b) Lam, L. S. M. and W. K. Chan, 2001. *Chem. Phys. Chem.*, **2**, 2557–2559.
120. Sakaki, S., T. Kuroki, and T. Hamada, 2002. *Dalton Trans.*, 840–842.
121. (a) Ferrere, S. and B. A. Gregg, 1998. *J. Am. Chem. Soc.*, **120**, 843–844; (b) Ferrere, S., 2000. *Chem. Mater.*, **12**, 1083–1089; (c) Ferrere, S., 2002. *Inorg. Chim. Acta*, **329**, 79–92.
122. (a) Yang, M., D. W. Thompson, and G. J. Meyer, 2000. *Inorg. Chem.*, **39**, 3738–3739; (b) Yang, M., D. W. Thompson, and G. J. Meyer, 2002. *Inorg. Chem.*, **41**, 1254–1262.
123. Wróbel, D., J. Lukasiewicz, J. Goc, A. Waszkowiak, and R. Ion, 2000. *J. Mol. Struct.*, **555**, 407–417.
124. Fungi, F., L. A. Otero, L. Sereno, J. Silber, and E. N. Durantini, 2000. *J. Mater. Chem.*, **10**, 645–650.
125. Nogueira, A. F., A. L. B. Formiga, H. Winnischofer, M. Nakamura, F. M. Engelmann, K. Araki, and H. E. Toma, 2004. *Photochem. Photobiol. Sci.*, **3**, 56–62.
126. Nogueira, A. F., L. F. O. Furtado, A. L. B. Formiga, M. Nakamura, K. Araki, and H. E. Toma, 2004. *Inorg. Chem.*, **43**, 396–398.
127. (a) Mitschke, U. and P. Bäuerle, 2000. *J. Mater. Chem.*, **10**, 1471–1502; (b) Silver, J., 2004. In Comprehensive Coordination Chemistry II., vol. **9**. pp. 689–717, eds. McCleverty, J. A. and T. J. Meyer, Elsevier-Pergamoni, Oxford, U.K.
128. Selected recent examples: (a) Muckl, A. G., S. Berleb, W. Brutting, and M. Schwoerer, 2000. *Synth. Met.*, **111**, 91–94; (b) Xie, W. F. and S. Y. Liu, 2003. *Semicond. Sci. Technol.*, **18**, L42–L44; (c) Zhang, Y. G., Y. F. Hu, J. S. Chen, Q. G. Zhou, and D. G. Ma, 2003. *J. Phys. D: Appl. Phys.*, **36**, 2006–2009;

(d) Xie, W. F., S. Y. Liu, and Y. Zhao, 2003. *J. Phys. D: Appl. Phys.*, **36**, 1246–1248; (e) Duan, Y., Y. Zhao, G. Chen, W. L. Jiang, J. Li, Z. J.Wu, J. Y. Hou, and S. Y. Liu, 2004. *Semicond. Sci. Technol.*, **19**, L32–L34.

129. Tokito, S., K. Noda, H. Tanaka, Y. Taga, and T. Tsutsui, 2000. *Synth. Met.*, **111–112**, 393–396.
130. Leung, L. M., W. Lo, Y. S. K. So, K. M. Lee, and W. K. Choi, 2000. *J. Am. Chem. Soc.*, **122**, 5640–5641.
131. Chen, Z. J., J. S. Yu, M. Sone, S. Miyata, Y. M. Lu, and T. Watanabe, 2001. *J. Phys. D: Appl. Phys.*, **34**, 2679–2682.
132. (a) Wu, A., D. Yoo, J.-K. Lee, and M. F. Rubner, 1999. *J. Am. Chem. Soc.*, **121**, 4883–4891; (b) Ng, W. Y., X. Gong, and W. K. Chan, 1999. *Chem. Mater.*, **11**, 1165–1170; (c) Ng, P. K., X. Gong, S. H. Chan, L. S. M. Lam, and W. K. Chan, 2001. *Chem. Eur. J.*, **7**, 4358–4367.
133. Cunningham, G. B., Y. Li, S. Liu, and K. S. Schanze, 2003. *J. Phys. Chem. B*, **107**, 1259–12572.
134. (a) Carlson, B., G. D. Phelan, W. Kaminsky, L. Dalton, X. Jiang, S. Liu, and A. K.-Y. Jen, 2002. *J. Am. Chem. Soc.*, **124**, 14162–14172; (b) Ranjan, S., S.-Y. Lin, K.-C. Hwang, Y. Chi, W.-L. Ching, C.-S.Liu, Y.-T. Tao, C.-H. Chien, S.-M. Peng, and G.-H. Lee, 2003. *Inorg. Chem.*, **42**, 1248–1255; (c) Xia, H., C. Zhang, X. Liu, S. Qiu, P. Liu, F. Shen, J. Zhang, and Y. Ma, 2004. *J. Phys. Chem. B*, **108**, 3185–3190; (d) Yang, J. and K. C. Gordon, 2004. *Chem. Phys. Lett.*, **385**, 481–485.
135. Welter, S., K. Brunner, J. W. Hofstraat, and L. De Cola, 2003. *Nature*, **421**, 54–57.
136. (a) Handy, E. S., A. J. Pal, and M. F. Rubner, 1999. *J. Am. Chem. Soc.*, **121**, 3525–3528; (b) Gao, F. G. and A. J. Bard, 2000. *J. Am. Chem. Soc.*, **122**, 7426–7427; (c) Buda, M., G. Kalyuzhny, and A. J. Bard, 2002. *J. Am. Chem. Soc.*, **124**, 6090–6098; (d) Gao, F. G. and A. J. Bard, 2002. *Chem. Mater.*, **14**, 3465–3470.
137. (a) Tsuboyama, A., H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, and K. Ueno, 2003. *J. Am. Chem. Soc.*, **125**, 12971–12979; (b) Duan, J.-P., P.-P. Sun, and C.-H. Cheng, 2003. *Adv. Mater.*, **15**, 224–228; (c) Laskar, I. R. and T.-M. Chen, 2004. *Chem. Mater.*, **16**, 111–117; (d) Slinker, J. D., A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, and G. G. Malliaras, 2004. *J. Am. Chem. Soc.*, **126**, 2763–2767; (e) Namdas, E. B., A. Ruseckas, I. D. W. Samuel, S.-C. Lo, and P. L. Burn, 2004. *J. Phys. Chem. B*, **108**, 1570–1577.
138. Tsuzuki, T., N. Shirasawa, T. Suzuki, and S. Tokito, 2003. *Adv. Mater.*, **15**, 1455–1458.
139. Ren, X., B. D. Alleyne, P. I. Djurovich, C. Adachi, I. Tsyba, R. Bau, and M. E. Thompson, 2004. *Inorg. Chem.*, **43**, 1697–1707.

140. (a) Kwong, R. C., S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest, and M. E. Thompson, 1999. *Chem. Mater.*, **11**, 3709–3713; (b) Guo, J., K. Ye, Y. Wu, Y. Liu, and Y. Wang, 2003. *Synth. Met.*, **137**, 1075–1076; (c) Che, C.-M., Y.-J. Hou, M. C. W. Chan, J. Guo, Y. Liu, and Y. Wang, 2003. *J. Mater. Chem.*, **13**, 1362–1366; (d) Lu, W., B.-X. Mi, M. C. W. Chan, Z. Hui, C.-M. Che, N. Zhu, and S.-T. Lee, 2004. *J. Am. Chem. Soc.*, **126**, 4958–4971.
141. (a) Christou, V., O. V. Salata, T. Q. Ly, S. Capecchi, N. J. Bailey, A. Cowley, and A. M. Chippindale, 2000. *Synth. Met.*, **111–112**, 7–10; (b) Curry, R. J. and W. P. Gillin, 2001. *Current Opinion in Solid State and Materials Science*, **5**, 481–486; (c) Kido, J. and Y. Okamoto, 2002. *Chem. Rev.*, **102**, 2357–2368.
142. Schanze, K. S., J. R. Reynolds, J. M. Boncella, B. S. Harrison, T. J. Foley, M. Bouguettaya, and T.-S. Kang, 2003. *Synth. Met.*, **137**, 1013–1014.