Current advances in fused tetrathiafulvalene donor-acceptor systems

Journal:	*Chemical Society Reviews*
Manuscript ID:	CS-REV-07-2014-000255.R1
Article Type:	Tutorial Review
Date Submitted by the Author:	25-Jul-2014
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Chem Soc Rev
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Cite this: DOI: 10.1039/c0xx00000x
www.rsc.org/xxxxxx

Tutorial Review

Current advances in fused tetrathiafulvalene donor-acceptor systems

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Abstract

Electron donor (D) and acceptor (A) systems have been studied extensively. Among them, fused D-A systems have attracted much attention during the past decades. Herein, we will present the evolution of tetrathiafulvalene (TTF) fused D-A systems and their potential applications in areas such as solar cells, OFETs, molecular wires and optoelectronics just to name a few. The synthesis, electrochemical, photophysical and intrinsic properties of fused D-A systems will be described as well.

Key learning points

- An overview of the applications in which fused donor-acceptor systems can be employed.
- Synthetic methods and strategies for obtaining and characterizing TTF fused donor-acceptor molecules.
- The electrochemical/redox properties of fused donor-acceptor compounds. With discussion on how this relates to electron-transfer and other processes.
- The photophysical attributes of donor-acceptor systems; such as charge-separated states and electron/energy transfer rates.

1. Introduction and applications

Fused electron donor-acceptor (D-A) systems have attracted intensive research in the past couple of decades. This review is part of a themed issue on the topic of molecular wires. Although our work has applications in such systems, the focus will be on fused electron D-A systems namely ones that involve tetrathiafulvalene (TTF) moieties. As a case in point, Fig. 1 shows a fused tetrathiafulvalene-benzothiadiazole (TTF-BTD) D-A molecule. In its partially oxidized state, interesting properties have been demonstrated such as acting as conductive molecular wires.[1] Single crystals with a highly symmetrical molecular structure can be grown and a novel case arises whereby the wires formed by regular π-stacks of TTF$^{+0.5}$ bear compactly bonded BTD acceptors representing localization of the LUMO along their ridges (Fig. 1).

The past decades have witnessed a substantial amount of research dedicated to studying the many derivatives of TTF compounds, mostly focusing on the synthesis, electrochemical and spectroscopic characterization of TTF with alkene-type carbon linkers between the TTF donor and acceptor moieties. Only relatively recently has the interest been aimed at fused D-A TTF derivatives bearing fully π-conjugated heteroatom systems. Herein, we aim to provide a synopsis on the evolution of D-A systems within our research group as well as a broader evaluation of some fundamental chemical and physical properties that fused D-A systems bear. These D-A systems have potential applications in artificial photosynthetic processes, photovoltaic devices, molecular electronics, polymer based solar cells, organic semiconducting materials, organic conductors[2] (see references therein) and materials possessing nonlinear optical properties.[3]

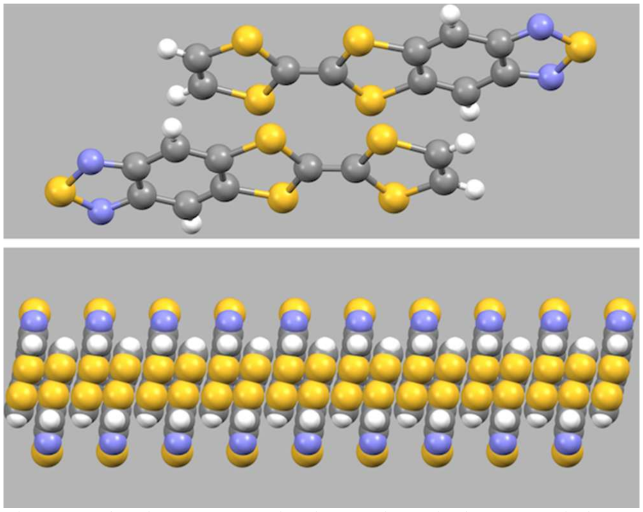


Fig. 1 Two fused TTF-BTD molecules are shown in the top panel; they π-π stack in a head-to-tail manner. Bottom panel: the partially oxidized TTF-BTD molecules with π-stacked orientation in the crystalline {(TTF-BTD)$_2$I$_3$} salt.[1]

Engineering of any fused D-A system must consist of the merging of an electron-rich donor and an electron-deficient acceptor. Interesting properties may be achieved by the fusing of donor and acceptor moieties such as the production of an energetically low-lying intramolecular charge-transfer state, extending the effective conjugation length and affording highly polarizable molecules. Furthermore, combinations of D and A units or fused D-A systems can be used in the preparation of segregated or non-segregated[1] charge-transfer salts for organic conductors and superconductors; for more reading on TTF and multifunctional materials see references and references therein.[1,2,4]

Typically, these materials are organized *via* weak supramolecular interactions, such as van der Waals forces, hydrogen bonding and π-π interactions in the solid state. By fusing molecular donor and accepter moieties together one forms a rigid aromatic structure, which can help to reduce reorganization energy, enhance the intermolecular π-π interaction as well as dipole-dipole interactions. Therefore, this class of molecules can play an important role in the field of organic field effect transistors (OFETs) as components of *p*-type or ambipolar semiconductors.

Aromaticity plays a crucial role in fused D-A systems, especially when the TTF donor is involved. Let's take a moment and review the criteria for the definition of how a molecule is classified as aromatic. First, the structure of the molecule is of great importance, it must be "flat" *i.e.* coplanar with all of the atoms within the molecule lying on the same plane as well as being cyclic in geometry. Second, all atoms must be conjugated with one another to yield a delocalized π-system with an arrangement of alternating single and double bonds. Lastly, it must contain $4n + 2$ delocalized π-electrons where n is zero or any positive integer, this is known as Hückel's rule. Aromatic compounds tend to be thermodynamically more stable than their saturated counterparts due to the delocalization of the electron density by resonance, thereby lowering the energy of the system.

The verb fuse, by definition, means to join or coalesce to form a single entity. This concept has been utilized to yield molecules that have new and interesting properties that differ from those of their counterparts alone. By fusing two individual molecules, in which, each bears a different property one may form a single molecule bearing a synergistic mixture of the new properties. The chemistry term, annulation, is used when a new ring is formed from a chemical reaction. By utilizing annulation one may fuse together molecular donor and acceptor moieties to form an extended π-system. This is of great interest, for example, when compact molecules are desired that have a small HOMO/LUMO gap (HLG) for the potential use in molecular electronics and optoelectronics. In order to achieve a system such as this, a donor molecule with a high-lying HOMO and an acceptor molecule with a low-lying LUMO must be fused in such a way to prevent too strong an electronic interaction between the donor and acceptor moieties that would render them neither strong donors or acceptors. To combat this issue of strong electronic interactions and to keep the HOMO of the donor and the LUMO of the acceptor localized, donor and acceptor moieties are often linked via flexible or rigid σ-spacers (D-σ-A).[5] One question that arises when considering the combination of donor and acceptor moieties using a π-linker (D-π-A) is how much the HLG will increase due to mixing of the respective HOMO and LUMO levels. Liu *et al.*[6] aimed to gain more insight into this question by synthesizing a fused D-A system containing the strong electron donor, TTF, and a strong electron acceptor in form of a TCNQ-type bithienoquinoid molecule (Fig. 2).

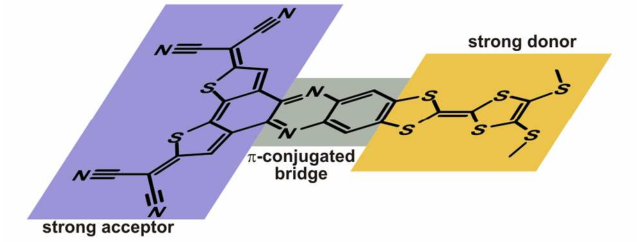


Fig. 2 Molecular structure of the fused TTF-TCNQ-type-bithienoquinoid and the highlighted regions of the electron donor, π-conjugated bridge and the electron acceptor. Reprinted with permission from ref. 6, copyright 2009, Wiley-VCH.

Annulation of these two redox-active components provided a D-π-A triad with a rigid and planar structural configuration as well as a well-defined molecular symmetry. The combination of these properties helps to maintain the location of the donor HOMO and the acceptor LUMO within discrete positions of the triad, thereby maintaining a small HLG of ~0.5 eV; this was determined by cyclic voltammetry, electronic absorption and time-dependent DFT calculations, see reference[6] for full detail. See references[7] for more in-depth reading on molecular structure and HOMO/LUMO relationships in π-conjugated systems. The interested reader may find more information on conjugated TTF-A systems and TTF π-donors for charge-transfer materials in references.[8]

Nature utilizes molecules that possess small HLGs to absorb light in the visible-NIR region of the solar spectrum. Such examples include chlorophylls, carotenoids and phycobilisomes (a light harvesting antennae of photosystem II), just to name a few, which are found in natural photosynthesis.[9] In order to achieve small HLGs these molecules have a high amount of conjugation, usually provided by numerous double bonds both in linear (carotenoids) and cyclic configurations (chlorophylls). This tends to yield rather large molecules, which nature has engineered and utilized in an elegant and efficient manner. Some artificial systems do not have the luxury of accommodating such large molecules but still need the small HLG and/or the ability to absorb visible-NIR photons. To illustrate the "molecular size" *vs* HOMO/LUMO tuning, (i.e. band gap, optical absorption) the absorption spectra of TTF, anthracene, β-carotene and a compact fused D-A molecule are shown in Fig. 3.

An important aspect to take from Fig. 3 is the drastic difference in the optical absorption between the D-A system and the anthracene molecule, which are relatively similar in length. For an example of longer conjugation, the absorption spectrum is shown for β-carotene, which has intense absorption bands between 400-500 nm. Although the length of conjugation in β-carotene is approximately 12 Å longer than in the fused D-A system the absorption is blue shifted by approximately 200 nm. Even though all are conjugated, the addition of hetero-atoms within the donor and acceptor units have modified the HOMO and LUMO energy levels such that a photo-induced intramolecular charge transfer (ICT) may occur thereby red-shifting the optical absorption to a large extent. Because of the fused D-A systems being able to absorb in the visible region they have been utilized in photovoltaic applications and have gained much attention. For instance, conjugated polymers with a low bandgap were developed by incorporating fused D-A moieties, as exemplified by recently reported polymers containing fused D-A dithienopyrrolobenzothiadiazole and dithienopyrroloquinoxaline arenes for use in a photovoltaic device with a power conversion efficiency (PCE) of 3.4%.[10] Moreover, fusing electron-deficient nitrogen heterocycles to the TTF skeleton can enhance the stability and charge mobility of the resultant organic D-A molecules. Taking all these advantages into consideration, TTF-fused poly(aryleneethynylene) systems were reported.[11] However, these conjugated polymers show a relatively poor photovoltaic efficiency. Recently, Liu *et al.*[12] have reported a quinoxaline-fused TTF D-A system, which was used in a dye-sensitized solar cell (DSSC) and produced a PCE of 6.5%. As seen in Fig. 4 when compound **1** is adsorbed onto a TiO_2 electrode with chenodeoxycholic acid (CDCA) (red curve), a coadsorbent for preventing aggregation, an incident photon to current efficiency value of ~70% is achieved in the region of 500-600 nm of the solar spectrum, as compared to without CDCA (black curve) which gave an IPCE of ~60%.

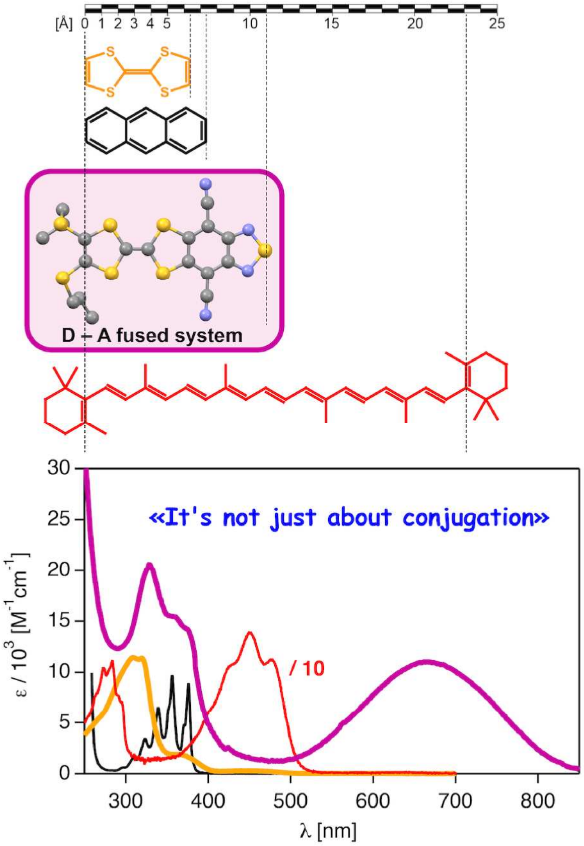


Fig. 3 Comparing conjugation length with optical absorption. The fused D-A molecule is from reference.[13]

For TTF sensitized solar cells this represents the best performance to date. In 2010 Wenger *et al.* demonstrated the usefulness of TTF based solar cells with a PCE of 3.8%.[14] Some drawbacks to using the TTF core as dyes in DSSCs are: (*i*) they absorb in the UV region of the solar spectrum; (*ii*) their redox properties are unfavorable because of their low oxidation potentials, *i.e.* energetically high-lying HOMO, and the driving force for the reduction of the oxidized TTF (after the forward electron injection) by the redox mediator I^-/I_3^- is minimal, therefore impairing the performance of the DSSC. In the aforementioned TTF-sensitized solar cell these drawbacks were minimized by stabilizing the HOMO level and extending the optical absorption over a wide range because of the intense light-induced intramolecular charge transfer arising from the annulation of the D and A moieties to form a rigid and planar D-π-A ensemble.

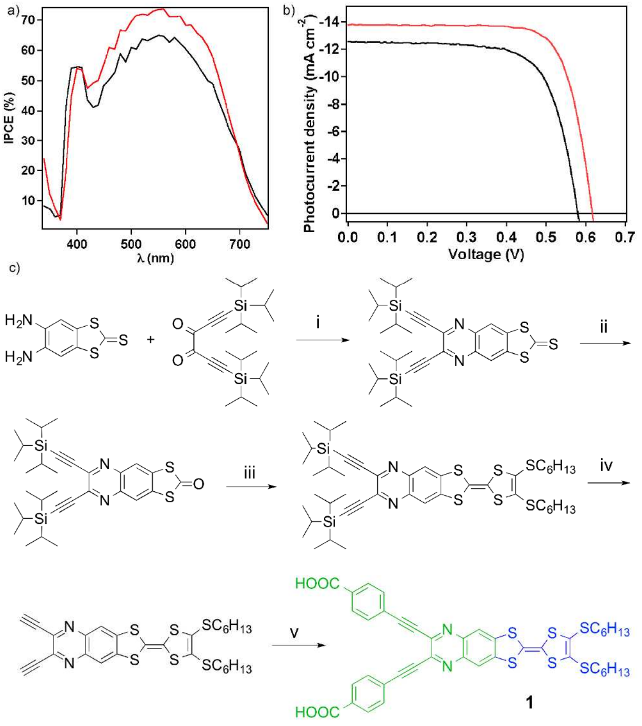


Fig. 4 Photovoltaic performance of **1** with (red) and without (black) a CDCA coadsorbent and synthetic scheme. (a) Photocurrent action spectra showing the incident photon-to-current conversion efficiency as a function of wavelength. (b) Photocurrent density (*J*) as a function of voltage (*V*) measured under standard air mass 1.5 and simulated sunlight at 1000 W/m^2 intensity. (c) i) ethanol, reflux, 68%; ii) mercuric acetate, CH_2Cl_2, 98%; iii) 4,5-bis(hexylsulfanyl)-1,3-dithiol-2-thione, triethylphosphite/toluene, 130 °C, 71%; iv) tetrabutylammonium fluoride, THF, -88 °C, 93%; v) 4-iodobenzoic acid, $Pd(PPh_3)_2Cl_2$, diisopropylamine, 80 °C, 12%. Data from reference.[12]

2. Synthetic methodology

The TTF building block has four primary positions in which chemical modifications may take place, those being the 4,5 and 4',5' carbons which allow one to synthesize symmetric or asymmetric TTF donor constructs (Fig. 5A). To obtain the TTF building block one begins with the 1,3-dithiol-2-ylidene precursor and their phosphonium derivatives. Other precursors include, disubstituted (at the 4,5-positions) 1,3-dithiol-2-thione which can be reacted with disubstituted (at the 4',5'-positions) 1,3-dithiol-2-one to yield the TTF donor core with a wide variety of substituent's, see reference and references therein for a detailed summary of the synthesis of TTFs.[4b,15,16] Great attention has been aimed on obtaining π-extended TTF compounds. The TTF core offers two synthetic routes to obtain such compounds, the 4,5 carbons and at the 2-position. Many examples may be seen where

π-systems such as phenyl, naphthyl or anthracenyl are introduced between the dithiafulvalene (DTF)[15] units (Fig. 5B, red). We will predominantly focus on the synthesis and applications of TTF π-extended systems where the π-extension is off of the 4,5- and 4',5'-positions of the TTF backbone (Fig. 5B, blue).

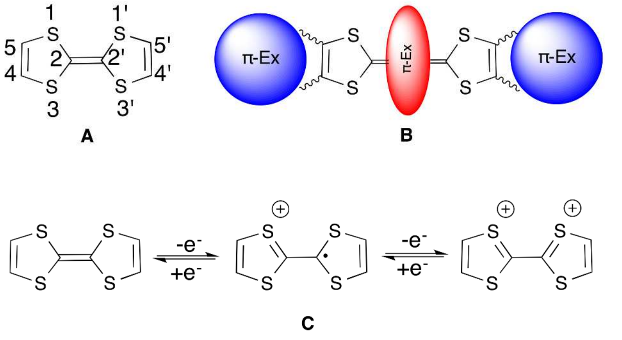
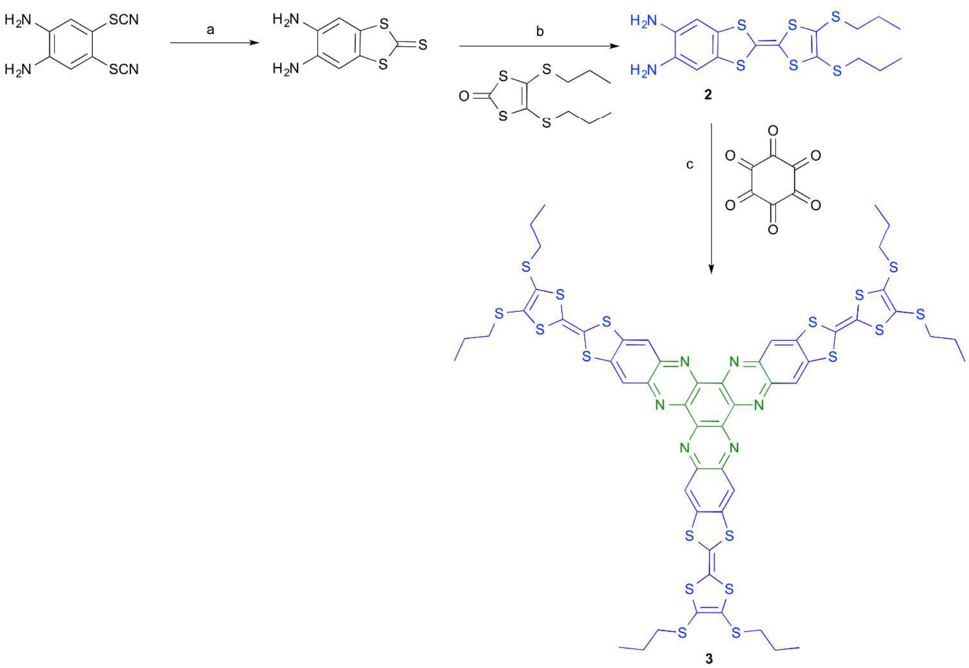


Fig. 5 Part **A** shows the TTF core with numbering system. In part **B** shows the different π-extension possibilities for the TTF core. Part **C** shows the resonance structures involved for the formation of the radical cation and further oxidation to form the dication species.

The electrochemical properties of TTF are unique in that a reversible, two-step oxidation may be observed *via* cyclic voltammetry. The first step forms a stable radical cation, which may be further oxidized to the dication (Fig. 5C). It is important to note that the TTF core in its ground state is not aromatic because of the 14 π-electrons, or 7 π-electrons for each 1,3-dithiol-2-ylidene ring (2 for each sulfur atom and 1 for each sp^2 carbon atom). Thus, oxidation converts a ring to an aromatic 6 π-electron configuration rendering good thermodynamic stability of its oxidized species. An interesting example of how the redox properties of TTF may be utilized was demonstrated by Chen *et al.* in which the authors used TTF as a redox mediator in charging of a Li-O_2 battery,[17] as well as examples from Kato *et al.* with rechargeable batteries.[18,19]

The predominant reaction/synthetic methodology used to prepare the majority of the fused TTF-D-A systems presented within this review is the Schiff base reaction. For further reading on synthetic methodologies that yield TTF fused ligand systems refer to references[20,21] and references therein. Schiff bases fall under the theme of carbonyl chemistry in that one of the reagents must be an aldehyde or ketone, one of these can then be reacted with either an aryl or aliphatic amine in an acid or base catalyzed reaction. It is important to note that Schiff bases involving aryl substituents are more stable and more easily synthesized. In the first step of the mechanism the amine acts as the nucleophile, which attacks at the carbonyl carbon to give an unstable intermediate called a carbinolamine. This intermediate then undergoes acid catalyzed dehydration to yield the imine or Schiff base. Our group has utilized this very powerful reaction to combine the diamine precursor **2** with a large variety of diketone compounds to formulate an extensive library of fused D-A systems. At the heart of this chemistry lies the Schiff base formation reaction. The first example of the utilization of Schiff base chemistry is shown in Scheme 1, reaction c, in which the diamine **2** was reacted with hexaketocyclohexane octahydrate in acetic acid to yield compound **3**.[22] The formation of the hexaazaphenylene (HAT) unit within compound **3** (Scheme 1, green atoms) gave two important properties of the molecule, (*i*) the HAT unit is an electron deficient π-system which enables three reversible reduction transitions in addition to the six-electron oxidations from three TTFs, (*ii*) it provides three potential metal binding positions.



Scheme 1 Synthesis of compounds **2** and **3**: a) $Na_2S{\cdot}9H_2O$, CS_2, H_2O, 50 °C, 52%; b) 4,5-bis(propylthio)-1,3-dithiole-2-one, triethylphosphite-toluene, 120 °C, 37%; c) hexaketocyclohexane octahydrate, acetic acid, 120 °C, 60%. In blue, are the electron donor units and green represents the acceptor unit.[22]

3. Metal ion binding motifs

To investigate how metal ion binding and oxidation may affect optical properties, $FeCl_2$ (metal ion source for binding) and $Fe(ClO_4)_3$ (chemical oxidant) was added, in different experiments, to a solution of compound **3** and monitored by UV-vis spectroscopy. See reference[22] for further details, as well as the work by Liu *et al.* for details of derivatives of compound **3** (with different alkyl chains) being studied on highly oriented pyrolitic graphite using scanning tunneling microscopy (STM) and spectroscopy (STS).[23] These results, in conjunction with the production of the useful diamine compound **2** lead to the preparation and investigation of compounds **4** (Fig. 6), **5**, **6** and **7** (Scheme 2). Compound **4** is prepared by fusing two heterocyclic compounds, TTF and dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz), more specifically compound **2** was annulated with 1,10-phenanthroline-5,6-dione in ethanol at reflux. Compound **4** shows electronic properties that are distinguishable from the two building blocks (TTF and dppz). Let's look at the electrochemical/redox potentials of compound **2**, its first oxidation ($E_{1/2}$) is 0.36 V *vs* Ag/AgCl and second is 0.73 V *vs* Ag/AgCl with no reduction signal; now we compare the redox potentials of compound **4**, its first oxidation ($E_{1/2}$) is 0.73 V *vs* Ag/AgCl and second is 1.08 V *vs* Ag/AgCl with a reduction at -1.17 V *vs* Ag/AgCl (Fig. 6).[24]

Notice that with the introduction of the dppz acceptor, the fused system is now harder to oxidize, presumably due to the electron-withdrawing character of the phenazine group. In addition, a reduction signal is now present in the fused system, which was not observed for the TTF precursor **2**. As seen in Fig. 7 compound **4** shows a strong absorption band at ~26,800 cm^{-1} (~375 nm) and a broad band centered in the visible region at ~18,500 cm^{-1} (~540 nm) which is due to the CT state that forms from the intramolecular electronic transition of TTF → dppz. The corresponding CT fluorescence with large solvent dependent Stokes shifts in different solvents is observed, showing that the excited state is more stabilized with more polar solvents, which is to be excepted and this result is corroborated with others in literature.[25] Because of the unique design of the dppz, it gives a metal binding site which was utilized by the chelation of Fe^{2+} and Zn^{2+} and monitored via spectroscopic techniques, see reference[24] for further details. Taking into account the interesting opportunities for different metal coordinations of compound **4**, it was used as a starting material to develop Ru^{2+} based TTF-dppz constructs **5**, **6** and **7**, as seen in Scheme 2.[26] Two synthetic methodologies were used to obtain these compounds, (*i*) chloride displacement using the TTF-dppz (**4**) and (*ii*) condensation, *via* Schiff base chemistry, of diamine **2** with Ru^{2+} centers decorated with phendione groups to yield the annulated TTF-dppz directly on the Ru^{2+}.

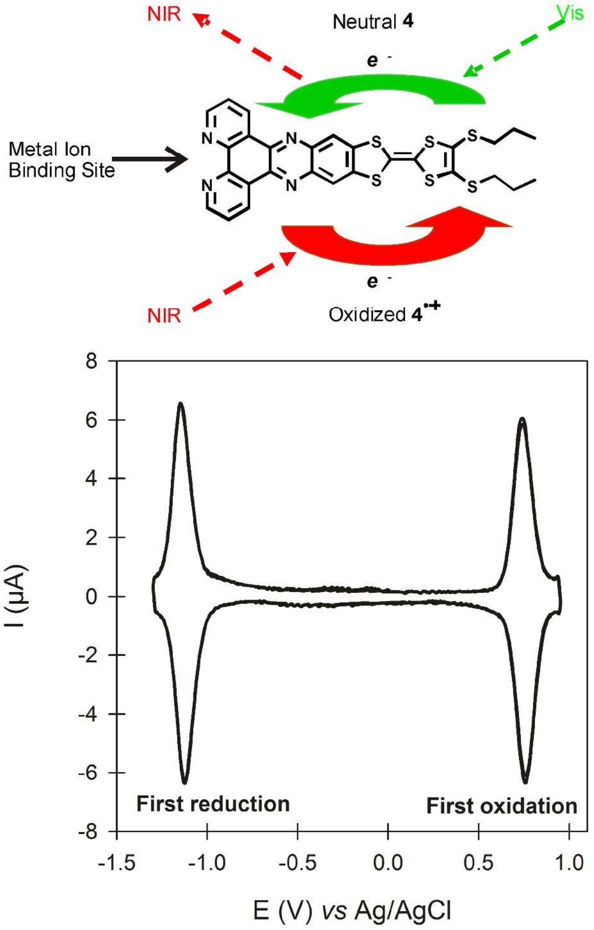
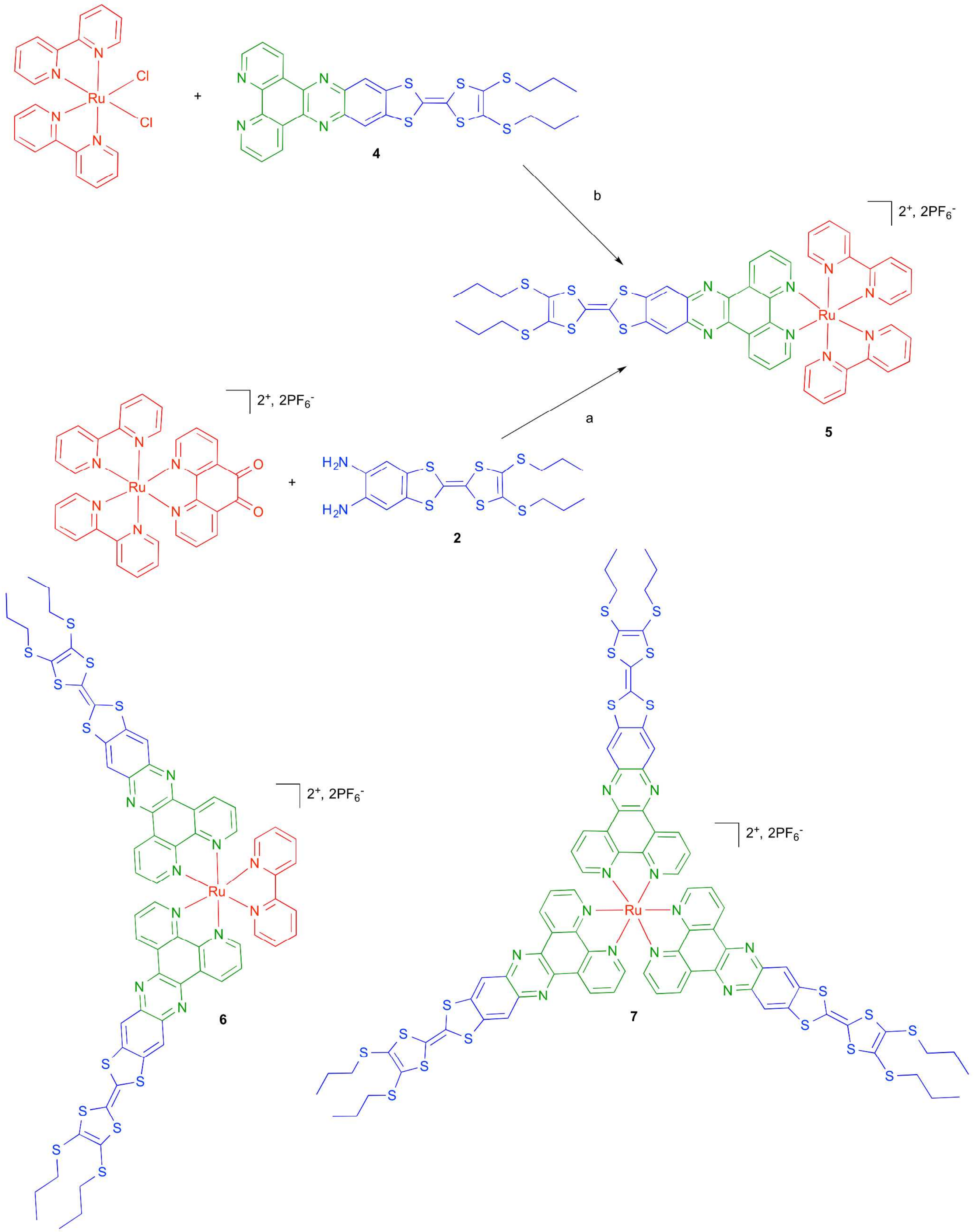


Fig. 6 (top) The fused D-π-A compound **4** with a metal ion binding site and extended optical absorption in the visible region of the solar spectrum with NIR fluorescence. (bottom) Thin-layer cyclic voltammetry of **4** in CH_2Cl_2. Adapted with permission from ref. 24, copyright 2007, Wiley-VCH.

The first approach is convenient when introducing ligands with good solubility in organic solvents but when incorporating rigid and planer ligands the solubility may be problematic, therefore the second approach, in some cases, may be beneficial.



Scheme 2 Synthetic strategy for obtaining compounds **5**, **6** and **7**: a) **2**, EtOH, reflux, 16 h; b) **4**, EtOH/H_2O, reflux, 16 h. Note, in order to obtain **6** and **7** one needs to start with the corresponding $[Ru(bpy)_{3-n}(phendione)_n]^{2+}$ precursor. The electron donor units within the molecules are shown in blue, green represents acceptor units and red is the Ru^{2+} core.[26]

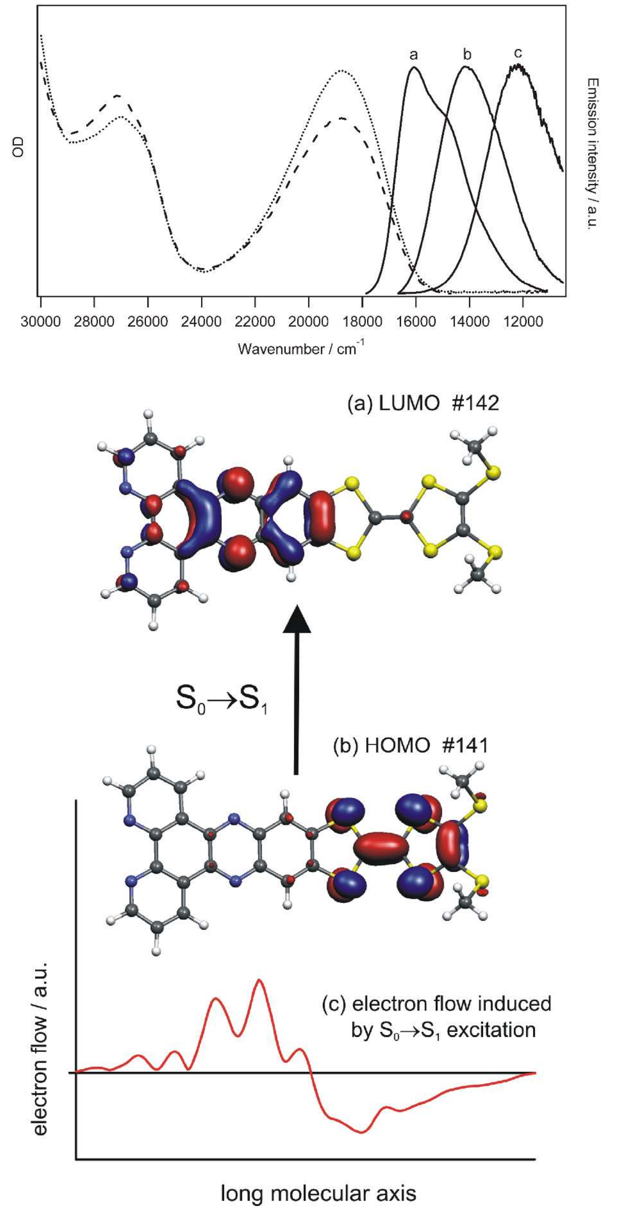


Fig. 7 (top) Emission spectra (solid lines, ν_{ex} = 18518 cm^{-1}, λ_{ex} = 540 nm) of the TTF-dppz (**4**) in different solvents at room temperature, a) cyclohexane, b) toluene, c) dichloromethane, and absorption (dotted line) and excitation spectra (dashed line, ν_{ex} = 13888 cm^{-1}, λ_{ex} = 720 nm) of **4** in toluene. (bottom) Electron flow induced by the light-induced ICT ($S_0 \rightarrow S_1$ ~540 nm), corresponding to the one-electron HOMO (D) → LUMO (A) promotion. Adapted with permission from ref. 24, copyright 2007, Wiley-VCH.

Compounds **5**, **6** and **7** all show clear intraligand charge-transfer bands centered around 16,000 cm^{-1} (625 nm) as seen in Fig. 8, which are attributed to a *π*-*π** transition and are red-shifted with respect to the ILCT transition of free TTF-dppz **4** (~18,500 cm^{-1}, 540 nm) because the energy of the LUMO localized on the dppz is lower upon coordination to the Ru^{2+} center. Furthermore, the coordination of more than one of ligand **4** (TTF-dppz) to one Ru^{2+} center results in a linear increase of the molar absorption of the TTF-dppz ILCT band. Electric-dipole-allowed metal-to-ligand charge-transfer bands are observed as well, these are located ~22,000 cm^{-1} (~455 nm) and arise from Ru^{2+} → bpy and Ru^{2+} → dppz transitions. Compounds **5**, **6** and **7** all show characteristic ILCT excited states. In **6** and **7** the ^{3}MLCT is strongly quenched due to electron transfer from a second TTF-dppz ligand to Ru^{3+} to form a charge-separated state, TTF-dppz^{-}-Ru^{2+}-dppz-TTF^{+}. The lifetime of this ligand-to-ligand charge-separated state (LLCS) is ~2 μs at room temperature (Scheme 3), see references for in-depth details.[26,27] This LLCS is long-lived presumably due to the spatial separation of the charges located on different ligands as well as the Ru^{2+} acts as a "blocker" for charge recombination.

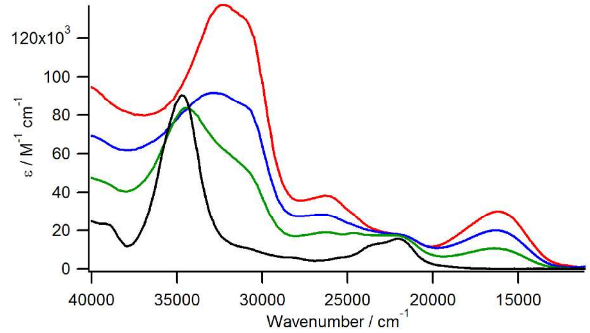
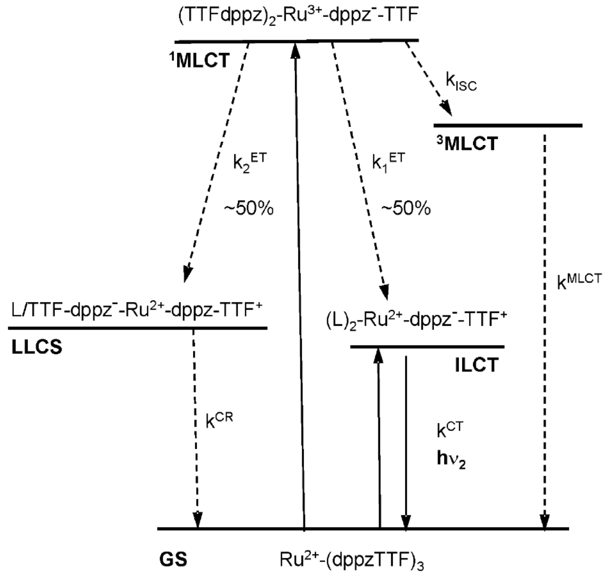


Fig. 8 Absorption spectra of **5** (green), **6** (blue), **7** (red) and [Ru(bpy)$_3$](PF$_6$)$_2$ (black) in CH$_2$Cl$_2$.[26]



Scheme 3 Energy level diagram showing the electronic ground state, excited states and the possible electron-transfer pathways along with relative rates of Ru^{2+} complex **7**. Adapted with permission from ref. 26, copyright 2007, Wiley-VCH.

Along this line, more work on ruthenium complexes has been reported either by the chemical modification of the *π*-linkers between TTF and phenanthroline units[28-30] or by the variation of the aromatic heterocyclic nitrogen-donor chelating ligand.[31] For example, the expansion of multiple ruthenium centers was achieved by the introduction of the dipyrido[2,3-*a*:3',2'-*c*]phenazine (ppb) unit in place of the dppz unit[31] or the incorporation of the additional dppz unit,[30] as illustrated in Fig. 9. Substituting an anthraquinone (Aqphen) for one of the TTF-dppz ligands to form a complex of [Ru(TTF-dppz)$_2$(Aqphen)]$^{2+}$ was engineered for the directional light-induced electron transfer from the TTF moiety to the electron accepting quinone.[32] This constitutes an important property for potential applications in solar energy conversion and signal processing.

Besides ruthenium coordination complexes, the binding ability of TTF ligands with a fused D-A structure to *d*-metal ions has also been explored for the development of dual-property molecular materials exhibiting the enhancement of π-d interactions.[33,34] It has been demonstrated that TTF-based ligands act as efficient charge-transfer antennas for the sensitization of Yb^{3+} and Er^{3+} NIR luminescence[35,36] and a dinuclear Dy(III) complex bearing two electroactive functionalized TTFs behaves as a single molecule magnet.[37] Consequently, synthesis, structures and properties of some lanthanide complexes with TTF-dppz have been described.[38]

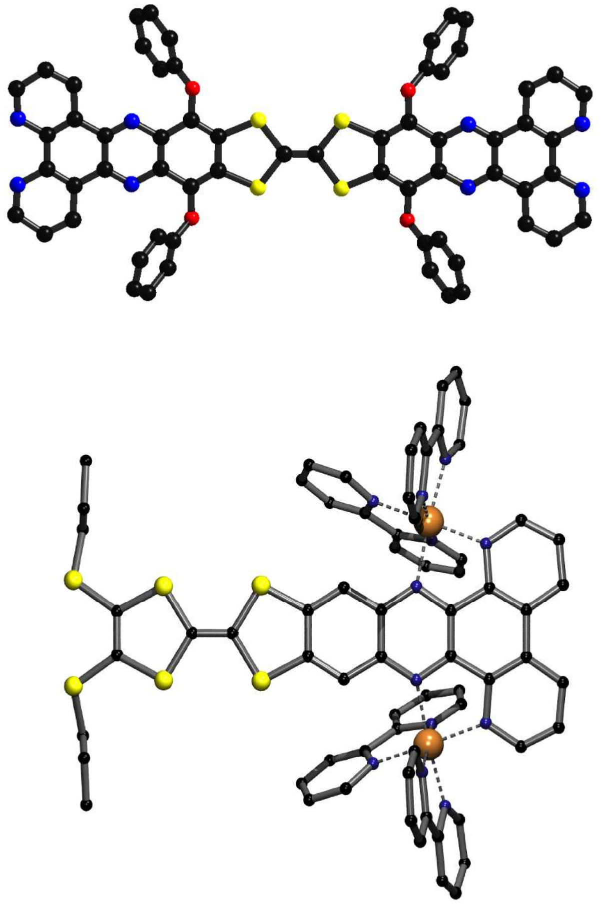


Fig. 9 Two types of di-metal binding TTF fused D-A systems.[30,31] Top structure demonstrates symmetrical metal ion binding with TTF donor in the middle. Reprinted with permission from ref. 30, copyright 2014, Wiley-VCH. The bottom structure shows a TTF donor with asymmetrical metal ion binding bays. Reprinted with permission from ref. 31, copyright 2008, American Chemical Society.

4. Chemosensors, nanographene and macrocycles

Annulated compound **8** (Fig. 10) was shown to behave as a chemosensor for fluoride ions. Upon F$^-$ binding to the pyrrolic units characteristic absorption and electrochemical shifts were observed.[39] Park *et al.* reported an example of annulated TTF-calix[4]pyrrole receptors as colorimetric chemosensors for nitroaromatic based explosives. Moreover, this class of artificial receptor has displayed biomimetic positive homotropic allosterism (binding a molecule at the protein's allosteric site) for binding of different guests.[40]

Another example of the multiple uses of fused TTF units may be found with compound **9** (Fig. 10) which comprises of a nanosized fragment of graphene (coronene) which is largely extended by annulation with multielectron π-donor TTF units to yield a deeply purple-colored, thus strongly chromophoric species, that absorbs in the visible region of the solar spectrum down to 750 nm.[41] This concept was then further elaborated upon with the synthesis of compound **10**, which bears two "donor-nanographene" units, two acceptor units and a donor-TTF core as seen in Fig. 10. Compound **10** was synthesized with use of a tetraamine precursor, which is an analog of compound **2**, and a tetrabenzovalene-1,2-dione unit in a Schiff base condensation; see reference for complete synthetic details.[42] The compounds in Fig. 10 are just a small example of the many annulated molecules that may be prepared using the classical Schiff base mechanism to yield multi-functional compounds.

Liu *et al.* reported a phthalocyanine (Pc) construct bearing a fused dipyrido[3,2-*f*:2',3'-*h*]quinoxaline (dpq) unit for chelating metal ions, in particular, ruthenium, and the spectral properties were investigated as well as the synthetic methodology to obtain such Pc-fused metal binding ensembles (see reference for further information regarding the photophysical and electrochemical properties).[43] An example of a fused TTF-Pc was reported by Liu *et al.* in which the authors used a tetra-TTF substituted Pc in order to study photoinduced intramolecular interactions within supramolecular systems. Based on this study, quenching of the Pc fluorescence by the TTF units was observed. This quenching is a result of a rapid intramolecular electron transfer between the excited singlet state of the Pc and the TTF. An interesting result from these studies shows that the fluorescence of the ZnPc-(TTF)$_4$ is sensitive to the oxidation of the TTF unit, all four of the TTF units must be oxidized in order for the luminescence from the Pc core to become efficient. Based on these findings, such systems may be utilized as efficient fluorescent redox switches, see reference[44] for details.

TTF annulated porphyrins (Por) have been in the crosshairs of researchers recently, in order to study the interesting multi-chromophoric properties. One such example is shown in Fig. 10 compound **11**,[45] wherein a TTF donor unit is annulated to the β positions of the porphyrin macrocycle. Chemical oxidation with [Fe(bpy)$_3$](PF$_6$)$_3$ was monitored via UV/vis/NIR absorption spectroscopy which showed formation of the TTF radical cation followed by a second oxidation of the porphyrin.

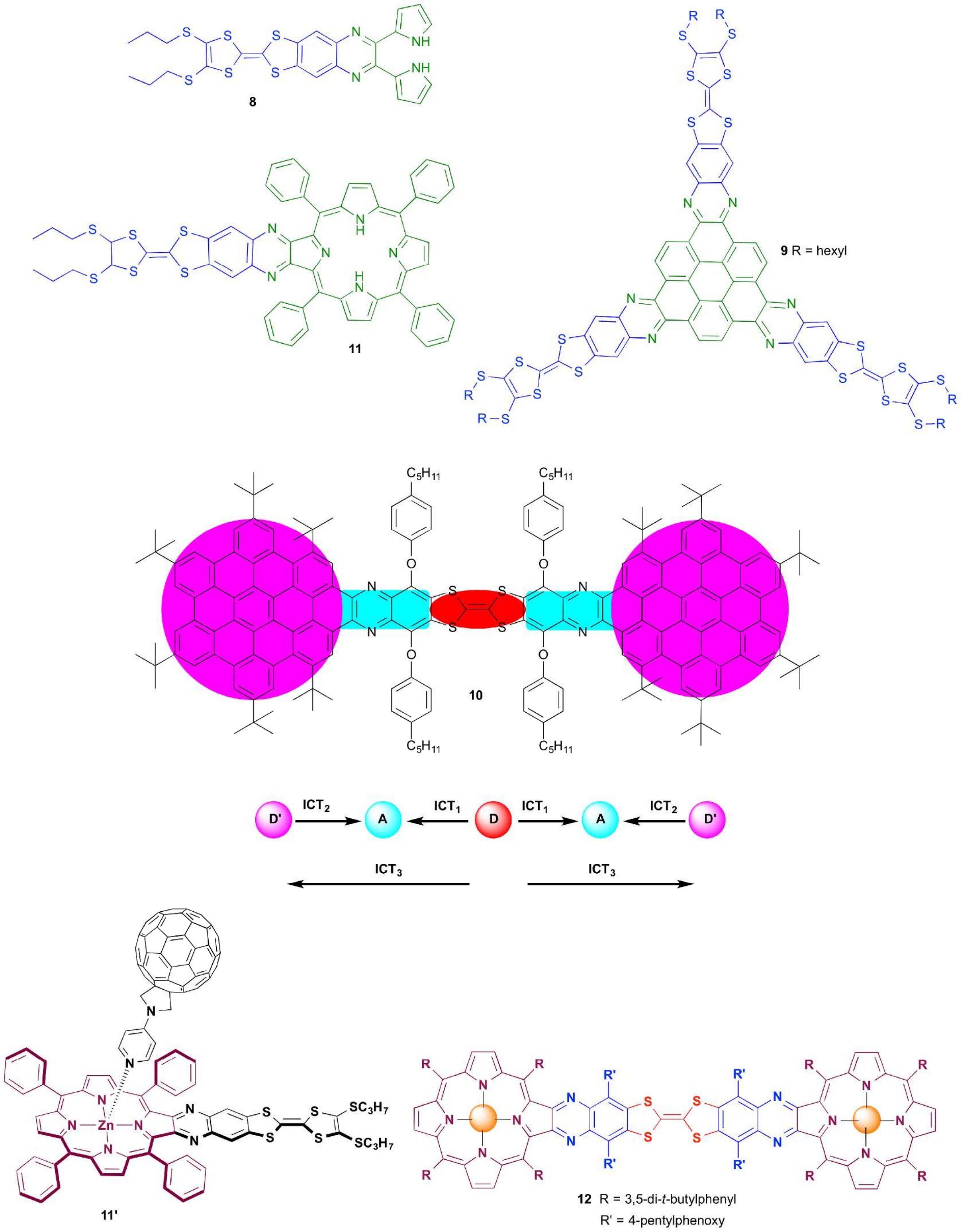


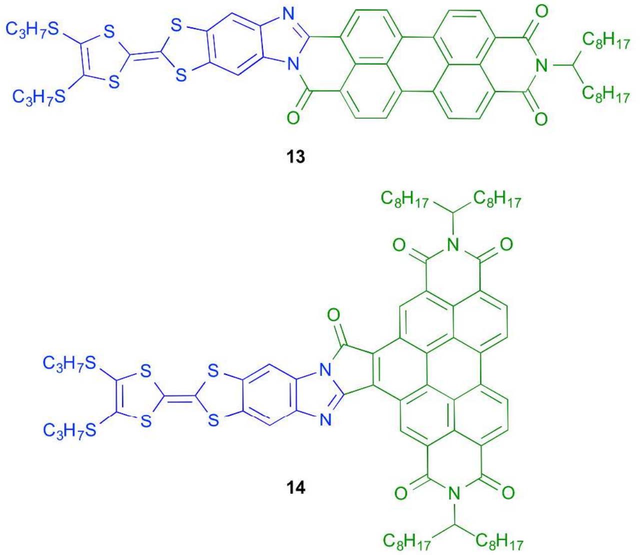
Fig. 10 Showing a variety of D-A systems. Compound **8** bears two pyrrole units for binding ions.[39] A tri-star shaped D-A ensemble is shown by compound **9**.[41] A multiple (pentad) D-A conjugated polycyclic aromatic hydrocarbon nanographene based system is represented by compound **10**. Reprinted with permission from ref. 42, copyright 2011, Wiley-VCH. Compound **11** is a TTF fused porphyrin.[45] Triad molecule **11'** with axial C_{60}py unit coordinated to a central Zn metal ion in the TTF-Por.[45] Compound **12** is a pentad as well, but substituted with freebase or metal porphyrins.[45]

To study a triad, TTF-Por compound **11** was functionalized with an axial N-pyridyl-3,4-fulleropyrrolidine (C_{60}py) electron acceptor coordinated to a central Zn ion within the macrocycle to yield compound **11'**. By introducing the electron acceptor C_{60}py a new electron-transfer pathway is therefore possible. The electron transfer from the TTF-Por to the C_{60}py was determined from spectroscopic studies. The optical absorption showed a bathochromic shift of the porphyrin Soret band upon addition of C_{60}py. The axial binding was further confirmed with fluorescence spectral changes, in which upon increasing amounts of C_{60}py the observed fluorescence counts decreased. This is due to quenching of the porphyrin fluorescence from the C_{60}py to yield [(ZnPor-TTF)$^{\bullet+}$-C_{60}py$^{\bullet-}$], the ZnPor radical cation and the C_{60}py radical anion. The kinetics of these electron-transfer pathways was resolved using transient absorption spectroscopy on the femtosecond timescale. These spectra showed a decrease of the singlet excited state of the Por-TTF (~540 nm) and simultaneously an increase in a new signal around 1000 nm, this is characteristic of the $C_{60}py^{\bullet-}$ radical anion; for detailed information on these studies see reference.[45] Symmetrically fused multiple D-A systems have received much attention with researchers. Compound **12** was prepared in order to study the electrochemistry and photophysics of a pentad D-A system. As seen in Fig. 10, compound **12** bears two porphyrin macrocycles which are fused through π-extended rings to the central TTF core. Within this construct are two porphyrins (purple) fused together by two quinoxaline electron acceptors (blue) through the central TTF donor (red). As a reference compound, **11** was crystallized and X-ray crystallography was done to show an almost perfect alignment along the Por-TTF axis in an alternating head-to-tail fashion with the TTF group of one molecule overlying the porphyrin unit of another one.[45] Quantum-chemical calculations were carried out in order to determine energies, intensities and the types of electronic excitations of compound **12**.[45] Jana *et al.* reported the preparation of directly fused TTF-Por systems, in which the authors functionalized pyrrole with TTF and subsequently reacted this with pyrrole and pentafluorobenzaldehyde in a standard Lindsey type porphyrin condensation reaction to yield mono-, di-, tri- and tetra-fused TTF porphyrins.[46] The authors then used the TTF-Por constructs for X-ray crystallography and extensive studies involving electrochemical and steady-state absorption and fluorescence techniques. Other studies involving an expanded porphyrin namely, a TTF-annulated *meso*-aryl[28]hexaphyrin(1.1.1.1.1.1) have been carried out. Interestingly, this molecule demonstrates different intramolecular charge transfers which are conformation-dependent and this dependency may be controlled by the choice of solvents, see reference[47] for full details.

Compound **13**[48] (Fig. 11) was prepared from a condensation reaction with the mono-anhydride perylene core and the diamine precursor **2**. As seen in Fig. 11 compound **14**[49] was synthesized in a similar fashion as **13** but the position of the anhydride was located on the bay-position of the perylene core. Both of the presented annulated TTF-PDI constructs provide intense optical absorption bands over a wide spectral range. Interestingly, the absorption spectra of the TTF-PDIs depend on the oxidation state. The TTF units can be oxidized to the $TTF^{\bullet+}$ radical cation by chemical oxidation, thus yielding red-shifted ICT bands as evidenced in both **13** and **14**. Compound **13** has successfully been used as a solution-processed active material for light sensitive field-effect transistors with balanced hole and electron mobilities.[50]

5. Conclusions and closing remarks

As demonstrated within this tutorial review, many fundamental scientific aspects have been discovered, leading to an extensive library of molecular systems and literature. The topic of developing molecular systems capable of bearing super/semiconducting, charge transfer and separation, near IR absorption and other useful properties is a rapidly growing field of research. We envision that fused D-A systems will play a major role in these developments and applications. It is normally the case within science that one needs to understand the fundamental knowledge of a system before one can implement it into an application based system. Fused D-A systems are now on this border of progressing into application based systems, as evidenced by recent use, just to name a few, in DSSCs, OLEDs, organic metals, and molecular electronics. Herein, we have presented the organic chemistry techniques, namely the Schiff base condensation reaction, which can yield a variety of TTF-fused D-A molecules. The electrochemical properties and the multi-electron stepwise oxidations of TTF-fused D-A conjugates have been presented. By forming rigid and planar molecules that keep the HOMO and LUMO orbitals on the respective D-A moieties localized, one can utilize the resulting intraligand charge transfer for certain applications. Photophysics plays a critical role in the characterization of this class of compounds, optical absorption spectroscopy gives insight into the multiple electronic transitions possible such as the MLCT found in the Ru^{2+} and other metal ion binding complexes, monitoring chemical oxidation titrations and observing radical cations and anions formed from electron-transfer processes. The use of time-resolved spectroscopic experiments provides the lifetimes and kinetics of these processes. These experimental results may be further explained/understood with the aid of computational chemistry. We have presented a wide range of fused D-A systems consisting of asymmetric, symmetric, metal ion binding complexes and macrocyclic compounds. Each of these types of D-A systems has interesting and distinctive properties as well as bigger picture applications. Combining the knowledge from the individual scientific fields above to develop a synergistic/interdisciplinary method to further develop such systems in a rational, multifaceted manner is a crucial aspect of this research.



13

14

Fig. 11 Molecular structures of perylene diimide (PDI) cores with annulated TTF.[48,49]

Acknowledgements

We wish to thank the current and past members of the Liu/Decurtins group who have contributed to our studies of fused electron donor-acceptor compounds as well as all the Collaborators mentioned in the References. Financial support for much of the research described in this review was obtained from the Swiss National Science Foundation (current grant no. 200021-147143).

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