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Enhancing the power conversion efficiency of dye-sensitized solar cells via molecular plasmons

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We introduce a tactic for employing molecular plasmons to enhance solar-to-electric power conversion efficiency of dye-sensitized solar cells. We offer general design principles of dimeric dyes, in which a strong plasmonic interaction between two π -conjugated moieties is promoted. The π -stacked conformations of these dimeric dyes result in a desirable broadened absorption and longer absorption onset wavelength.

Solar cells deliver clean and renewable energy and are promising candidates for sustainable energy generation. Dye-sensitized solar cells (DSSCs),¹⁻⁵ in particular are increasingly popular due to their high stability, low cost, ease of production, and tunable working wavelengths that enable high power conversion efficiencies. To date, DSSCs have primarily been categorized into two groups, with ruthenium organometallic complex⁶⁻¹² based designs being employed more commonly than their donor- π -bridge-acceptor (D- π -A) counterpart dyes.³ DSSCs in the latter group, however, are attractive because they contain no precious (rare) ruthenium metal and are simpler to fabricate. Furthermore, the generally intense absorption of D- π -A dyes can support the use of thin TiO₂ films in portable DSSC devices.

The high performance of ruthenium-containing DSSCs can primarily be attributed to their wide absorption windows that extend to near-infrared (NIR) wavelengths.⁶⁻⁸ Hence, D- π -A dyes that absorb both broadly and strongly would substantially improve the performance of their associated DSSCs. Indeed, numerous reports in the literature focus on D- π -A dyes that exhibit a panchromatic absorption,^{3,13,14} or that use strategies such as co-sensitization^{3,15} and energy relay² to extend the absorption breadth of DSSCs. In this work, we propose a very general and simple alternative for broadening the absorption

and lowering the onset energy of D- π -A dyes through the use of molecular plasmonic interactions, which are free-electronlike collective excitations that can form in planar π -electron systems.¹⁶⁻²¹ Note that our aim is not to design specific dyes; rather, we formulate and validate general principles that can be used to both improve known and discover new dyes. We focus on the following criteria that are characteristic of efficient dyes:^{2,3,22,23}

(a) A long wavelength absorption onset along with (b) a broad and strong absorption spectrum. We will demonstrate that these two criteria can readily be achieved by constructing dimeric dyes, in which the two π -conjugated moieties interact strongly with each other and produce multi-peak plasmonic excitations.

(c) The LUMO of a dye should be localized on the anchoring group (acceptor) to promote an ultrafast electron injection and (d) the HOMO spatially removed from the TiO₂ surface to reduce the charge recombination via the dye (CR1). The two criteria can naturally be met if the dimeric dyes are constructed from those monomeric units that satisfy them.

(e) The formation of a (hydrophobic) barrier that prevents direct contact between the electrolyte and the TiO₂ to reduce charge recombination via the electrolyte (CR2). This can be realized, for example, by adding hydrophobic alkyl chains to the designed dyes.^{2,3,24,25}

(f) Oxidation potentials that allow for a small but sufficient loss-in-potential, thereby driving electron injection and the dye regeneration of the DSSCs. Introducing hexyl side-chains into the dyes can result in a change of the oxidation potentials that would breach the thresholds for efficiently driving the DSSCs. This can be resolved by adjusting the environment of the dye, e.g. the redox mediator,^{26,27} the solvent,²⁸ and/or various additives.³ In the present work the oxidation potentials of the dyes are tuned by inserting appropriate auxiliary functional groups.²⁹⁻³¹ quaterthiophene dimer results from the strong interaction between the plasmons of the two quaterthiophenes.

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[†] Footnotes relating to the title and/or authors should appear here.

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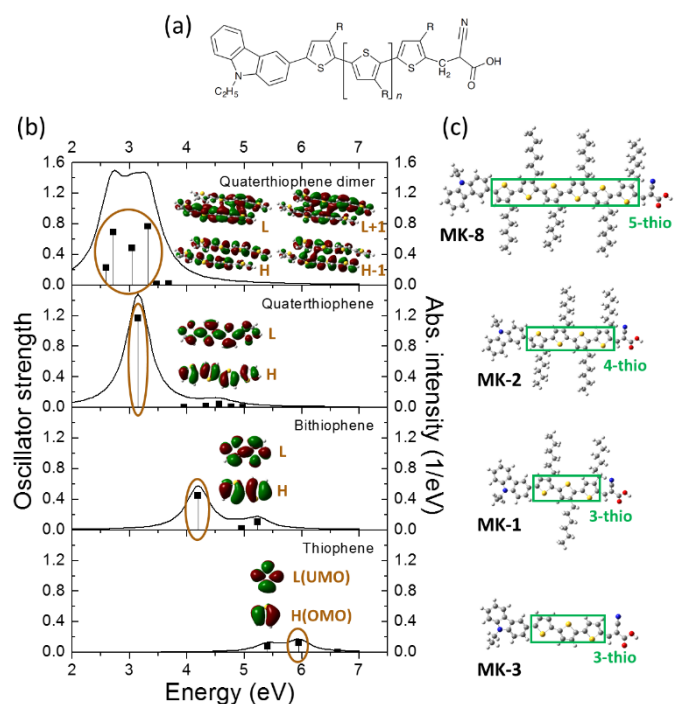


Fig. 1 (a) 2-dimensional molecular representation of the MK dye²⁴ featuring an oligothiophenes moieties. (b) Plasmonic excitations of mono- and oligothiophenes, computed at the ADC(2)/cc-pVTZ level. The multi-peaked absorption of (c) MK dyes relevant to the design of the dimeric dyes. Grey, blue, red, yellow, and white spheres denote carbon, nitrogen, oxygen, sulfur, and hydrogen atoms, respectively.

The computed absorption peaks of thiophene, bithiophene, and quaterthiophene, shown in Fig. 1b, reveal that the longer the oligothiophene molecule, the stronger its principal absorption peak (The computational details are presented in the ESI/Sec. 1.†). These peaks are associated with the $\Delta n=1$ (i.e., HOMO to LUMO) plasmonic excitation,¹⁶ as in a one-dimensional electron gas, where n corresponds to the number of nodes in the orbitals.¹⁶⁻¹⁹ Furthermore, a dimer of properly oriented oligothiophenes can result in a strong interaction of the monomers' plasmons (the uppermost panel of Fig. 1b), generating a multi-peaked absorption. Therefore, one can broaden the absorption of a dye by promoting a strong interaction between the plasmons-supporting π -conjugated systems, e.g. oligothiophenes. Within this perspective, we considered the MK-3 dye²⁴ (Fig. 1c), composed of a carbazole as the donor, cyanoacrylic acid as an acceptor and terthiophene as the π -bridge, as a good starting point for our design. MK-3 is known to exhibit a broad absorption spectrum on the TiO₂ surface due to the substantial π - π interactions occurring between neighbouring dyes. However, it suffers from significant charge recombination (CR), which is detrimental to the overall performance of the associated DSSC.

Introducing hexyl side-chains into MK-3 leads to MK-1²⁴ (Fig. 1c), in which the CR process is suppressed. Nevertheless, the bulky hexyl group cause lower TiO₂ surface coverage, which prevents efficient π - π interactions between the MK-1 molecules

and results in both a narrower absorption peak and an increased absorption onset energy compared to MK-3. Adding an extra thiophene unit to the π -conjugated oligomer of MK-1 gives MK-2²⁴ (Fig. 1c), whose absorption peak (with a similar width) and onset energy are both red-shifted with respect to MK-1 (Fig. 2a of ref. 24, See also Fig. S3† for the computed excitation energies and oscillator strengths, in vacuum, of the principal peaks of these dyes). In terms of solar-to-electric power conversion efficiency (IPCE), today MK-2 is considered to be superior to MK-3, despite its narrower adsorption.²⁴ With these results in hand, our immediate objective is to construct superior dyes that simultaneously retain the advantages of MK-3 [specifically its broad absorption with a high IPCE over a broad wavelength range due to strong π - π (plasmonic) interactions] and MK-2 (whose hexyl chains can reduce the CR rate of the respective DSSC).

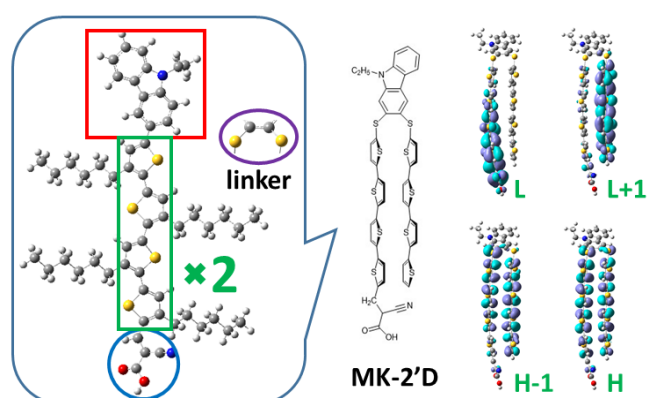


Fig. 2 A designed dimeric dye, MK-2'D, consisting of the donor (carbazole), acceptor (cyanoacrylic acid) and two quaterthiophenes (hexyl chains removed) of the MK-2 monomeric dye. The donor is linked to the π -conjugated oligomer via two sulfur atoms. The HOMO, HOMO-1, LUMO, and LUMO+1 of MK-2'D are also plotted (isovalue = 0.02).

The π -moieties of MK-2 and MK-3 (i.e. oligothiophenes), adopt various packing motifs depending on their lengths, sidechain substituents, etc. The cofacial π -stack, as discussed above, coincides with strong inter-bridge interactions that yield signature multi-peaked optical absorption and/or improved charge transport properties.³²⁻³⁶ To harness this property, we constructed a dimeric dye featuring two π -moieties attached to the same linker group, as illustrated in Fig. 2. The linker must permit a face-to-face stacking of the two π -conjugated moieties. In the designed MK-2'D dye, the (covalent) bonding between the donor and the two quaterthiophene units ensures favourable intramolecular stacking and, ultimately, an interaction superior to MK-2 (vide infra).²⁴ Thus, the flexible quaterthiophene bearing no acceptor group will naturally stack on top of the other oligomer, that will dock to the TiO₂ surface via the cyanoacrylic acid group. Several linkers, which ensure stable π -stacking, have been examined in Fig. S5.† The stability of the stacking conformation within MK-2'D is confirmed by molecular dynamics simulation at room temperature (see ESI/Sec. 7†). Hence, the same approach can be applied to those dyes that can accommodate two closely oriented plasmon-

supporting π -moieties through the use of appropriate linker groups.

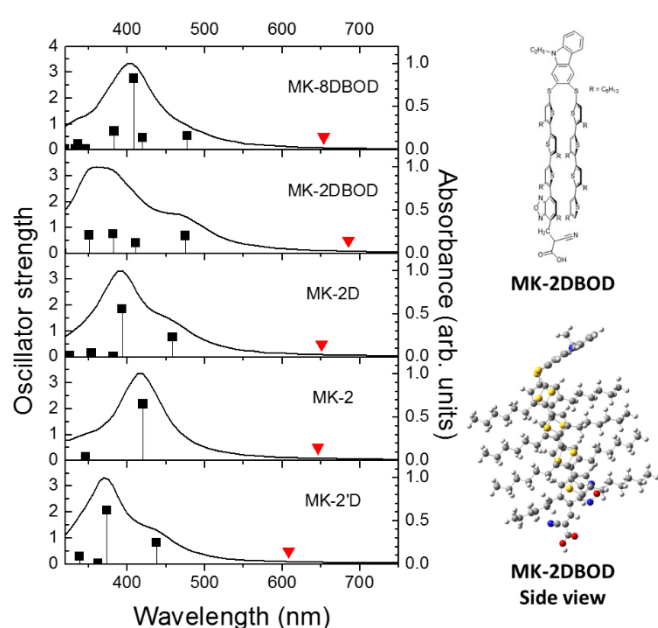


Fig. 3 Absorption wavelengths and oscillator strengths of the illustrative designed dyes, computed using TD- ω B97X-D/cc-pVDZ at the ω B97X-D/6-31G* optimized geometries. Computed absorbances (maximum height normalized to 1) of MK-2, MK-2'D, and MK-2DBOD (see also Fig. S10†) are also visible. The red triangles denote the onset wavelength, defined as the wavelength of 2.5% absorbance. MK-2DBOD retains the parallel arrangement of the π -conjugated moieties and exhibits a strongly broadened absorbance and decreased onset energy compared to MK-2.

Akin to the other MK dyes, the LUMO of MK-2'D (Fig. 2) favourably extends to the acceptor group (see ESI/Sec. 8†), whereas the HOMO-1 and HOMO do not. The HOMO-1 and HOMO originate, respectively, from the in-phase and out-of-phase linear combinations of the HOMOs of the constituent oligothiophenes. Most importantly, the computed absorption spectrum of MK-2'D (Fig. 3 and Fig. S10†) exhibits multiple peaks characteristic of the strong interaction of molecular plasmons with a substantially broadened width in comparison to MK-2.

It is worthwhile to note that dyes carrying two anchoring groups, rather than one (attached to each of the quaterthiophene moieties), no longer displayed multiple peaks (Fig. S10†) and, thus, were not identified as promising alternatives. In fact, this narrower absorption confirmed by MD simulations (Fig. S10†) was attributed to the misalignment of the π -conjugated moieties, caused by the interaction between the two anchoring groups (ESI/Sec. 8.7†). The π -stacking motif was also strongly distorted when clamping the two π -bridges at both ends, shifting the principal absorption peak (plasmons) toward larger rather than lower energies (ESI/Sec. 8.8†).

We then considered a MK-2D dye (in Fig. 3) substituted with hexyl chains,²⁴ which resulted in a breach of the threshold potentials (Fig. 4). As noted earlier, the proper redox properties

can be restored by introducing an electron withdrawing group, such as benzooxadiazole (BOD), to the dye.²⁹ The subsequent

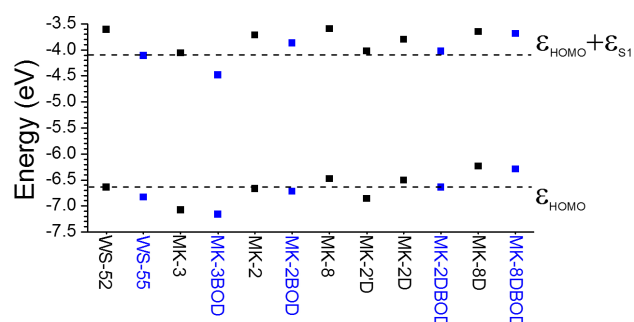


Fig. 4 Energy levels of GSOP (estimated by ϵ_{HOMO}) and ESOP (estimated by $\epsilon_{\text{HOMO}} + \epsilon_{\text{S1}}$) from TD- ω B97X-D/cc-pVDZ computations (gas phase) at the ω B97X-D/6-31G* optimized geometries. Upper and lower dash lines, set up according to the performances of WS-55 and WS-52 dyes in DSSCs²⁹ (see Section 8 in the ESI†) mark the thresholds for an efficient electron injection and dye regeneration, respectively. Blue font colour denotes the dyes featuring the auxiliary BOD group.

MK-2DBOD dye is formed by replacing a thiophene unit next to the cyanoacrylic acid group by the BOD group (Fig. 3). The latter favours the localization of the LUMO in the anchoring region; the position of the auxiliary group can be determinant for the performance of DSSCs.³⁰ We demonstrate that MK-2DBOD is stable under thermal motions (Fig. S9†). Moreover, as shown in Fig. 4, after inserting the BOD into MK-2D, the oxidative potential of both the ground and first singlet state decreases, with the GSOP aligning perfectly below the potential threshold for efficient dye regeneration. Finally, the absorption spectrum of MK-2DBOD (Fig. 3) is substantially broadened and the onset energy lowered in comparison to MK-2D. Thus, it is expected that MK-2DBOD would exhibit a substantially widened IPCE spectrum over the absorption wavelength.

As a proof of principle, we also considered a dimeric dye, MK-8DBOD, derived from MK-8. Its longer π -conjugated chains interact more strongly within the dimer and do result in stronger and more red-shifted absorptions, further boosting sunlight power conversion as shown in Fig. 3. Among other strategies,³ the oxidation potentials of the MK-8DBOD dye (Fig. 4) can be potentially adjusted by adding functional groups.^{3,29-31}

We demonstrated a very simple and general approach for broadening the absorption spectrum and lowering the absorption onset energy of (existing) monomeric D- π -A sensitizers by constructing dyes with two adjacent plasmon-supporting π -moieties that interact strongly with one other. Molecular plasmons of properly aligned π -conjugated oligomers will interact intensely to promote multi-peaked absorption. At finite temperatures, the absorption of most of the dye's accessible conformations will be split, resulting in a further broadened (Fig. S10†) absorption spectrum and decreased absorption onset energy compared to the monomeric precursor.

The effects of introducing (1) hexyl chains, (2) BOD (an electron-withdrawing group), or (3) more π -conjugated units to

these dimeric dyes were also examined. The use of longer π -conjugated chains produces an overall stronger absorption. On the other hand, the hexyl chains used to reduce the CR rate of the associated DSSCs can, at the same time, increase its HOMO level. This increase is overcome by inserting auxiliary group(s) such as BOD to the dye. Therefore, a judicious arrangement of molecular units within dye can ultimately afford the panchromatic light harvesting sensitizers, capable of delivering an efficient electron injection and dye regeneration and suppressing the charge recombination rate in the associated DSSCs.

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