Cite this: DOI: 00.0000/xxxxxxxxxx

Photo-excited Intramolecular Charge Transfer In Dye Sensitizers : Predictive In-silico Screening for Dye Sensitized Solar Cell Devices

Kalyani Chordiya^{1,2}, Md. Ehesan Ali³, Mousumi Upadhyay Kahaly^{1,2*}

Received Date

Accepted Date

DOI: 00.0000/xxxxxxxxxx

Efficient photo-induced intramolecular charge transfer (ICT) from donor to acceptor in dye molecules is the functional basis and key property in the working of dye-sensitized solar cell (DSSC). To understand the ICT process in photo-excited dye molecules, we analyse the electronic properties and structural parameters of a chosen set of experimentally synthesized donor-acceptor (D-A) and donor- π -spacer-acceptor (D- π -A) type dye molecules in their ground, excited and cationic states. The correlation between structural modification and charge redistribution in different parts of the molecule helps to identify the extent of π -conjugation and spatial rearrangement of electron density localization along the molecular skeleton. We find that prominent twisting of several groups and resulting molecular bond rearrangements in larger parts of the molecule promotes efficient donor to acceptor ICT, such as in D-A type, ADEKA1 and C275 dyes. Thus based on modest computation of structural and electronic properties of dye molecules in their respective ground, excited and cationic states, we identify the desired structural changes that facilitate tunable intramolecular charge transfer to highlight a simple and direct prescription to screen out probable efficient dye molecules among many samples. Motivated by recent experimental evidence of capturing the structural view of the excited-state charge transfer in molecules, we provide a fresh outlook towards predictive and systematic computational screening and design of dye molecules, complementing parallel experimental approaches in the development of state-of-the-art DSSC.

1 Introduction

Dye Sensitized Solar Cell (DSSC) were initiated after their first report by O'Regan and M. Grätzel in 1991¹⁻³, and with this rapid development was observed in the DSSC owing to their low-cost materials⁴, flexible designs⁵, high performance and stability under low or diffuse light conditions.⁶ The research efforts are mainly focused on tailoring the efficiency and stability by designing new sensitizer⁷⁻⁹, modifying the semiconductor bandgap^{10,11} optimizing the redox couple¹², dye absorbance¹³ and counter electrodes¹⁴. Typical working of the device starts with photo-excitation of the dye molecule (from Dye $\rightarrow$ Dye*/Dye⁺ in ns). The excited dye molecule (Dye*) will release an electron into the conduction band of the semiconductor material (in ps timescale) leaving the dye in cationic (Dye⁺) state.¹⁵ The released electrons from anode move through an external circuit, and reach the cathode in 10^{-8} - 10^{-1} s.¹⁶ Then the oxidized dye is regenerated when the dye

receives electrons from a redox mediator (I^-/I^{-3}) (μ s). Oxidation of medium happens in the process within ps-ns. Further, these oxidized redox mediators (I^{-3}) diffuse to the counter electrode, where it is regenerated by the electrons reaching the counter electrode through an external circuit. Thus, the dye and electrolyte solution regain original state and are ready to repeat the cycle. Working schematics of a typical DSSC with time scales involved in the electron transfer cycle of the device is given in Fig. 1(I). Thus it is obvious that the efficiency of the device is highly sensitive to the structure and performance of the dye molecules.¹⁷

The dye molecules typically of the donor-acceptor (D-A) and donor- π -acceptor (D- π -A) type, have attracted immense attention in the field of DSSC.¹⁸ The electron donating group with aromatic amines such as triphenyl amine¹⁹, carbazole²⁰ and triazatruxene²¹ owing to their high positive mesomeric effects, synthetic availability and modularity are best suited as donor groups. The π -spacer links the donor and acceptor group and has to have the electron affinity higher compared to donor and lower than the acceptor group.²² On photo-excitation of the dye, electron density of this molecule is rearranged and trapped by the highly electronegative groups such as π -spacer and acceptor group.²³

^a 1. ELI-ALPS, ELI-HU Non-Profit Ltd., Wolfgang Sandner utca 3., Szeged, H-6728, Hungary; E-mail: mousumi.upadhyaykahaly@eli-alps.hu

^b Institute of Physics, University of Szeged, Dóm tér 9, H-6720 Szeged, Hungary.

^c Institute of Nano Science and Technology, Mohali, Punjab 140306, India

* Corresponding author: mousumi.upadhyaykahaly@eli-alps.hu

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 00.0000/00000000.

SM-315 dye reported by the Mathew et al. with 13%³³ power conversion efficiency (PCE), ZL001 and ZL003 by Li Zhang et al. with 12.8% and 13.6% PCE respectively,²¹ are considered highly efficient D- π -A dyes. To improve the efficiency further there were variations in structure such as D-A, D- π - π -A, D-A'- π -A and D-D- π -A;^{34–36} changes in the donor in order to extend the π -conjugation,⁷ π -spacer bearing a strong electron donor group and high molar absorption coefficient^{8,37}, acceptor and linker as a stronger electron-withdrawing group^{9,38–41}. In addition to designing new dyes, new hole^{42,43} and electron^{44,45} transport materials were developed to show low glass transition temperatures, low melting points, and high solubility; leading to increase in pore filling into semiconductor film and increasing the surface area for adsorption of dye. At the end, semiconductor layer with high dye loading as well as high light harvesting efficiency capability will ensure the increase in photocurrent density and the improved performance of DSSCs.^{46,47} Hence, structural/ chemical/ electronic modifications in any of the components (like, D, π , A, linker, interface etc) and resulting electron transfer kinetics⁴⁸ changes the PCE significantly.

However, understanding the interplay of different physicochemical and photochemical aspects of the main components of DSSCs demands molecular level understanding of the dye molecules. This can be achieved by using quantum chemistry methods like density functional theory (DFT) and time-dependent density functional theory (TDDFT), which helped researchers find excellent agreement with experimentally reported geometries and electronic properties^{49,50}. DFT studies on a dye sensitizer molecule⁵¹ reveal their electron donating and withdrawing components which play an important role in understanding intramolecular charge transfer (ICT) after photo-excitation. Easier flow of π electrons from one conjugate part of the molecule to another part requires that the orbitals are extended through the atoms that make the conjugate system. This implies efficient charge delocalization, thereby improving the intramolecular charge transfer. Hence, the electronic structure of different ionized states of the molecules has to be calculated.⁵² Structural changes due to ICT is possible if the molecule is flexible to adapt the changes provided the π -conjugation is extended through donor, to acceptor. True ICT states reflect change in both electronic structure and molecular geometry, and often prominently differ from the ground states in their molecular structure⁵³.

ICT can be addressed in many ways, such as, by taking difference in charge density between two states, twisting of certain group in dye, or with fluorescence^{30,54}. Well-known for efficient ICT, fused molecules have been used in multiple recent studies for designing organic dyes including fused-ring (hereafter referred as fused) molecular structures as D, π -spacers to increase the performance of the dye^{55–57}. Fully fused molecules have planar backbones in all the electronic states, while the non-fused molecular framework usually allows structural distortion. Consequently, the fused ones tend to show higher reorganization energies, resulting in reduced voltage and current losses⁵⁸. Thus it is also important to identify the fused molecular groups in a dye molecule and correlate with its reorganization energy and extent of charge transfer.

Understanding of ICT in dye molecules (rather molecules in general) and its correlation to PCE is often captured through expensive simulations and resource-consuming experiments^{59,60}. Usually they involve molecular engineering, screening, strategies for suitable fabrication and optimization for higher effi-

ciency. During the process often issues like purification, tailoring the absorption band of sensitizer dye and cost effectiveness, are involved. The question remains, as from the huge number of available molecular dyes, how to screen out the ones that shows stronger tendency of high PCE?

In this report, based on DFT and TDDFT methods, we highlight the structural changes and resulting ICT in a dye molecule after photo-excitation ($\text{Dye} \rightarrow \text{Dye}^*/\text{Dye}^+$), as shown in Fig. 1(II and III). We choose six different dyes with different reported PCE (as in parenthesis) for comparison (shown in Fig. 1(II)(a-f)); ADEKA1 (12.8%)^{24,25}, C275 (12.5%)²⁷, C257 (8.7%)²⁹, D5L2A1 (6%)³⁰, CB4 (4.28%)³² and D5L2A3 (2%)³⁰. These dyes have been studied experimentally and are physically and chemically stable.

To observe the true ICT in these dyes and to correlate it with the experimentally reported PCE we use the following steps: (i) The optimized ground state geometry is used to simulate the UV-Vis spectra. (ii) Charge density difference for each transition state is observed. (iii) Then, we select the strongest excited state with lowest energy to relax the molecule in excited state. (iv) Next, an electron is removed from the system (to obtain Dye^+ , cationic state), and we relax the molecular geometry in that cationic state. (v) Similarly, one electron is added to the neutral geometry (to obtain Dye^-) and molecule in this anionic state is geometrically relaxed. (vi) Using the final energies of the dye molecule in its relaxed geometries in ground state, cationic and anionic states, the reorganization energy ($\lambda_{e/h}$) is calculated. (vii) The geometrical parameters of dye in ground, excited and cationic state are studied to identify the charge transfer and geometry modification.

As elaborated later in section 3, the analysis of the relaxed geometries in ground, excited and cationic states of a dye molecule guides us to identify the spatial charge redistribution by means of bond reorganization in different parts of the dye molecule. Note that consideration of cationic state helps to mimic the electron injection mechanism from the excited dye molecules into a wide band gap of semiconductor (like TiO_2) as usual in experiments.¹⁵ Finally, we correlate the efficiency of the dye to transfer the electron from donor to acceptor with the extent of molecular π conjugation and structural distortion and charge localization. This should assist the suitable structural engineering of organic dyes for more efficient photovoltaic performance.

2 Theoretical Methods and Computational Details

The calculations based on the description of the electronic ground state are given by solving time dependent Schrödinger equation given by Eq. 1 for which the Hamiltonian is described by Eq. 2,

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \hat{H} \psi(\vec{r}, t) \quad (1)$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}(\vec{r}, t) \quad (2)$$

with kinetic energy $\hat{T}$, electron-electron repulsion $\hat{V}_{ee}$ and the external potential $\hat{V}(\vec{r}, t)$. Probability of finding an electron at position r at time t is given by taking the absolute square of the wavefunction $\psi(r, t)$. Based on the Runge-Gross theorem, using the wavefunction, we can calculate the external potential which will produce the density for further analysis⁶¹. Simulations for the dye sensitizer under this study were performed using ORCA 4.0^{62,63} quantum chemistry package. The ground state

Fig. 1 (I) Schematics of DSSC with electron transfer process involved shown by black one direction arrows and the time scale for the electron transfer. (II) Structure and the experimentally reported power conversion efficiency (PCE) of dyes (a) ADEKA1 (12.8%)^{24,25}, (b) C275 (12.5%)^{26,27}, (c) C257 (8.7%)^{28,29}, (d) D5L2A1 (6%)^{30,31}, (e) CB4 (4.28%)³², (f) D5L2A3³⁰ (2%). The blue colour represents donor group, green as π -spacer linkage, and red as acceptor. (III) UV-Vis spectra (green curve) of ADEKA1 spanning over the spectral range of 220–700 nm, suggesting adequate light absorption, along with electron charge density re-localization in excited Dye (Dye*) corresponding to two peaks in UV-Vis. The Dye* isovalue shows the electron density on photo-excitation of the dye with particular frequency. Right panel shows structure or geometry change owing to Dye to Dye*/Dye⁺ transition, which occurs within nanosecond time scale¹⁵.

Dyes	fused D	fused π	fused A	λ_e	λ_h	λ	$\lambda' = \lambda_e - \lambda_h $
ADEKA1	yes	NA	no	0.4507	0.4441	0.8949	0.0066
C275	yes	NA	no	0.4077	0.4509	0.8587	0.0432
C257	no	NA	no	0.0416	0.2483	0.2900	0.2067
D5L2A1	no	no	no	0.4063	0.1808	0.5817	0.2255
CB4	yes	yes	no	0.3384	0.3014	0.6399	0.0370
D5L2A3	no	no	no	0.3523	0.2908	0.6431	0.0615

Table 1 Presence of fused D, π -spacer and A group in dye, calculated electron (λ_e) and hole (λ_h) reorganization energy, total reorganization energy (λ) and reorganization energy difference (λ') between λ_e and λ_h for ADEKA1, C275, C257, CB4, D5L2A1 and D5L2A3. ("NA" means not applicable)

molecular geometries of the dyes and their electronic structures were obtained with PBE0/def2-TZVP method^{64–66}. The electronic spectra of the dyes and excited state geometry optimization were performed using TD-DFT. PBE0 functional provides good description of both ground and excited states⁶⁷, whereas, with def2-TZVP basis set errors in bond length is smaller than 1 pm and in bond angles smaller than 1°^{65,68}. To reduce the computational time RJCOSX approximation is used in addition to replacing bulky alkyl groups in dye with smaller alkyl group. The large hexyl groups in ADEKA1 are replaced by ethyl groups; hexyl groups in C275 and C257 are replaced by methyl groups. Photo-absorption spectra was calculated with TDDFT approach including solvent effect to simulate the real experimental conditions; using conductor like polarizable continuum model (CPCM)⁶⁹. We calculate the energy gap (E_g) for a dye which is given as the ground state energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels ($E_g = E_{LUMO} - E_{HOMO}$). Change in dipole moment ($\Delta S = S_1 - S_0$) of the molecule on photo-excitation marks charge separation in the molecule. Singlet excitation state lifetime (τ) is expressed as $\tau = \frac{1.499}{f \cdot E^2}$ ⁷⁰; where E is excitation energy and oscillator strength f ; provides an estimate of the time for injection of electron from the dye to semiconductor substrate. Longer the excitation lifetime, higher is the optical stability of dye in that state.

Semi-classical theory of charge transfer rate equation has been developed by Marcus^{71–73} and quantum mechanically is given by Jorther et. al.^{74–76}. The electron transfer in non-adiabatic regime is considered to be analogous to an optical transition between two electronic states within Franck-Condon approximation⁷⁷. Rate of charge transfer is the probability of the electron transfer from the donor to acceptor per second. In the condition of maximum transfer rate we can consider Gibbs free energy is approximately equal to the reorganization energy (λ). The re-organization energy (λ) is given by $\lambda = \lambda_e + \lambda_h$; where $\lambda_i = (E_0^\pm - E_\pm) + (E_\pm^0 - E_0)$. E_0 and $E_\pm$ represent the energies of the neutral and cation or anion species in their lowest energy geometries, respectively, while $E_\pm^0$ and $E_0^\pm$ represent the energies of the neutral and cation species with the geometries of the cation or anion and neutral species

3 Results and Discussion

The ground state geometry and electronic structures of all six dye molecules as predicted by our calculations, show that the energy gap for the dyes lie in narrow range of 2.5–3.1 eV showing a reasonable match with the earlier reported results (see supplementary information SI Table S1). Hence, the choice of functional and basis set are suitable for the present study. The energy of HOMO of all dyes is lower than the redox potential of electrolyte (for I^-/I^{-3} is -4.8 eV)⁷⁸, ascertaining that the regeneration of the oxidized dyes are energetically favorable. We also find the LUMO of each chosen dye molecule to be above the conduction band edge position of semiconductor substrate (for TiO₂ semiconductor is -4.0 eV)⁷⁹ (see SI Table S1) which guarantees efficient electron injection from LUMO of the dye molecules to the conduction band of TiO₂.

Using TD-DFT and CPCM combined calculations, photo-absorption excited states were obtained with solvent effect as given in experimental studies (see SI Fig. S1). For example, toluene as solvent for ADEKA1^{24,25}, tetrahydrofuran (THF) solvent for C257²⁹ and C275²⁷, methyl chloride (CHCl₃) solvent

for CB4³² and methyl cyanide (MeCN) solvent for D5L2A1³⁰ and D5L2A3³⁰ have been used in our calculations (following given experimental references). The oscillator strength and excited state lifetime (τ), are tabulated in SI Table. S2. The photo-absorption spectra reveals that the first strong excitation is an outcome of the transition from ground to first excited state in case of ADEKA1 and C275, to second excited state for D5L2A1 and D5L2A3, third excited state for C257, and sixth excited state for CB4. The contribution of molecular orbital transitions in given excited state are tabulated in SI Table. S2. From SI Table. S2 we observe that ADEKA1 (at 643.5 nm), C275 (at 808.5 nm), C257 (at 671.5 nm), D5L2A3 (at 719.6 nm) show 90% HOMO → LUMO transition. Whereas, D5L2A1 (at 667.8 nm) show 97% HOMO-1 → LUMO+1 transition and CB4 (at 497.3 nm) show 25% HOMO → LUMO transition for the first strong excitation. Hence, it is worth noting that the first strong excitation does not necessarily originate mainly from HOMO → LUMO transition. In Fig. 2(a-f) we plot the charge density difference (with respect to the ground state) for the first strong excited states (as reported above) and observe, all six dyes show charge migration from donor group to acceptor group. To study, photo-excitation induced ICT and the modified molecular geometry of the dye molecule affect each other, we will optimize the excited state geometry of dyes in their first strong excited state (we will refer “first strong excited state” as “excited state” throughout this article).

A comparison of the dipole moment between the ground state and the excited state geometries of dyes is given in SI Table. S1. The dipole value for ADEKA1, C275 and D5L2A3 increases on transition from ground to excited state, suggesting possible prominent modification of charge densities and molecular structural parameters^{80,81}. On the contrary in case of C257 and D5L2A1 decrease in the dipole value is found, which could be due to electron density localized on group other than the acceptor⁸² after photo-excitation (see Fig. 2). In case of CB4 the geometry optimization calculations for excited state did not reach convergence; so, we keep CB4 out in our further discussions. Fig. 2(c) shows spatial localization of electron density in excited state is mainly on the benzothiadiazole unit which is far away from the substrate, when compared to its ground state charge distribution. Relatively small excited state dipole moment in C257 ($S_n=3.604$ Debye, as enlisted in Table S1, corresponding to the excitation with 671.5 nm) indicates small excited state charge separation. This suggest that excited state charge density localization could be used as one important and cheaper way to understand charge separation in excited state. This could also explain the decrease in dipole moment on excitation of C257 with 671.5 nm photon.

The increase in the dipole moment in excited state geometry shows prominent charge separations⁸², as also supported from our charge density distribution results for C275 (see Fig. 2(b)). Electron and hole reorganization energies (λ_i with $i = e$ for electron, h for hole) are other important parameters, showing the efficiency of the dye to transport hole or electron across the molecule. Note that, smaller difference in the electron and hole reorganization energy reveals the efficiency of the dye in transporting both charged particles with similar ease. In addition, analysis of the λ_i helps to choose the charge transport material.⁸³ Table. 1 shows ($\lambda_h < \lambda_e$) for D5L2A1, CB4 and D5L2A3 which show good hole transfer ability whereas, ($\lambda_h > \lambda_e$) for C257 show better electron transfer ability. ADEKA1 and C275 show small magnitude of λ' , i.e., small difference between λ_h

Fig. 2 Localization of hole and electron density on each dye in its excited state. (a) ADEKA1 show hole density (yellow colour iso-surface) on carbazole (donor) and first two thiophene and electron density (purple colour iso-surface) on cyanide and two thiophene groups (acceptor). (b) C275 show hole density on indenoperylene (donor) and electron density on ethynyl benzothia-di-azole-benzoic acid (acceptor). (c) C257 show hole density localization on triphenyl amine (donor) and electron density localized on benzo-dithiazole group (acceptor). (d) CB4 show hole density on carbazole (donor) and electron density on cyanoacetic acid (acceptor). (e) D5L2A1 have hole density on triphenyl amine (donor) and electron density on cyanoacrylate (acceptor). (f) D5L2A3, hole density on triphenyl amine (donor) and electron density on rhodanine (acceptor). [Atoms (colour): C (cyan), N (blue), O (red), S (yellow), H (gray), B (pink), Si (dark yellow)]

and λ_e , suggesting similar efficiency of these molecules in electron and hole transfer abilities (in comparison to other dyes). Presence of fused groups is known to affect ICT and reorganization energies owing to less distorted structures. However, they are also known to sometimes hinder the ICT process⁸⁴. To address the effect of presence and absence of fused groups at the donor and π -spacer sites (see Table. 1) we analyse the structural changes in the different parts of the dye molecules followed by photo-excitation and removal of electron simultaneously identifying the ICT pathway and extent of π -conjugation.

In Fig. 3 we show the difference in bond length between ground state and excited state geometry (red plot) and ground state and cationic state geometry (blue plot). Corresponding numbers for these bond length differences are listed in SI Table. S3 column ΔE and ΔC . The abbreviation for bond length between the atom type X and its index n (X_n) is given by $B(X_i, X_j)$, angle as $A(X_i, X_j, X_l)$ and dihedral angles as $D(X_i, X_j, X_l, X_k)$. The atomic indices for atoms in ADEKA1 except hydrogen in donor groups are from 48 to 62 for and acceptor from 0 to 47. Variation in bond length between $B(C48, C44)$ and $B(C50, C49)$ of donor group, $B(C44, C43)$, $B(C36, S35)$, $B(C22, S21)$, $B(C36, S35)$, $B(S31, C30)$ and $B(Si6, C5)$ in acceptor group show the extended conjugation in the ADEKA1 dye. Furthermore, a change in angles and dihedral angles in acceptor groups demonstrate delocalization of charge throughout the structure of ADEKA1 (see SI Fig. S4(a) for bonds angles, Fig. S5(a) for dihedral angles and Table. S3 for corresponding values). The overall effect of extended π -conjugation and delocalization of charge, as observed in molecular frame of the dye in excited and cationic states with respect to ground state (see Fig. 3 and Fig. 4), are summarized as follows. The alteration of the structural parameters for the entire molecule describes that the π -conjugation is extended in both excited and cationic state.

The distance between the nitrogen (blue atom) in the donor group to Si atom in acceptor group, increases as the structure evolves from ground (23.030 Å) $\rightarrow$ excited state (23.695 Å) $\rightarrow$ cationic state (23.772 Å). Finally we estimate the twist from the dihedral angle between the donor and the first thiophene of acceptor, and also between the last thiophene and phenyl-silyl-anchor (blue shade box in Fig. 4 for cationic state). ADEKA1 has a fused donor group (see Table. 1) and prominent variation is observed at the atomic sites of donor in the close vicinity of the oligothiophene in acceptor group ($B(C48, C44)$, $B(C50, C49)$, $D(C49, C48, C44, C43)$, $D(C49, C48, C44, S45)$). This shows that the fused rings are structurally stable on excitation and ionization. The oligothiophene, not being fused, shows variation along the complete structure and reflects the transfer of charge from one end of the dye to another. The distinctive twist of the phenyl-silyl-anchor in cationic state (highlighted box in Fig. 4) suggests a possibility for efficient charge transferred from the dye to semiconductor substrate.^{85–87}

Similarly, we study the optimized geometry of all the other molecules in the study in SI Fig. S3, S4, S5. The atomic indices (excluding hydrogen) for donor and acceptor parts of C275 are as follows: (i) in donor are from 0 to 41, (ii) 42 to 63. C275 show variation in the bond lengths along $B(C6, C5)$, $B(C14, C12)$, $B(C38, C32)$ and $B(O28, C9)$ of donor; $B(C44, C37)$, $B(C50, C49)$, $B(C60, C55)$ and $B(C61, C57)$ of acceptor (see SI Fig. S3(a) for bond lengths and corresponding values in Table. S4). However, major variations in the bond angles and dihedral angles are seen on the donor group (see SI Fig. S4(b) for bonds angles, Fig. S5(b) for dihedral angles and Table. S4). This is reflected in the Fig. S6(second column for C275) where, the cationic state geometry show twist in the donor along the link between donor and acceptor (see corresponding dihedral angle $D(C50, C46, C37, C36)$) when in excited state. In cationic

Fig. 3 Difference in bond length of ADEKA1 dye in excited (red) and cationic state (blue), with respect to ground state geometry. With difference ($\Delta > 0.01$ Å) are marked with "*". The red box highlights changes for acceptor group and blue box highlights change for donor group.

state a twist by 24.48° (D(C51,C46,C37,-C33)) between donor and acceptor, and by 21.76° (D(C59,-C55,C48,C47)) in acceptor is observed, resulting in a planar structure (SI Fig. S3(b) for bond lengths, Fig. S4(c) for bonds angles, Fig. S5(c) for dihedral angles and Table. S4). This favors the charge transfer from donor to acceptor. C275 has largest fused structure in donor part, however, prominent variation in bond length at B(C6,C5), B(C14,C12), B(C38,C32) and B(O28,C9) in donor shows less stable structure on the hand twisting in acceptor shows the transfer of charge between the rings.

The atomic indices (excluding hydrogen (H)) for C257 in its three parts are as follows: (i) in donor, carbon (C) from 6 to 45, nitrogen (N) 46, 47 and 29 and oxygen (O) 42, 43 and sulphur (S) 48, 53 and 52; (ii) in acceptor, C from 0 to 5, 49, and O 50, 51. In C257 the donor becomes planar in cationic state, however, the acceptor also goes out of plane with respect to the donor. This might affect the effective charge transfer to the substrate (SI Fig. S6(third row in third column for C257), SI Fig. S3(b) for bond lengths, Fig. S4(c) for bonds angles, SI Fig. S5(c) for dihedral angles and corresponding values in SI Table. S5). Variation of structural parameters in donor at site (B(C7,C6)) and non-fused site between cyclopentadithiophene and benzodithiazole (B(C16,C15)) after excitation, and at non-fused site B(C17,C16) after ionization along with twisting between the donor and acceptor) hints active charge transfer between the rings. Negligible structural variation inside the cyclopentadithiophene group reveals stable structure with minimal distortion which results in low electron recombination energy for C257 dye.

The atomic indices (excluding hydrogen) for D5L2A1 in its three parts are as follows: (i) donor are from 0 to 18, (ii) π -spacer from 19 to 25 and (iii) acceptor from 26 to 30. D5L2A1 show prominent bond length variation (change (Δ) > 0.02 Å with respect to ground state) on the entire molecule, however the dihedral angle varies mostly along the donor group (see

SI Fig. S3(c) for bond lengths, SI Fig. S4(d) for bonds angles, SI Fig. S5(d) for dihedral angles and values in SI Table. S6). In this system, electronic charges are mostly localized near donor, with negligible transfer to the π -spacer and acceptor (SI Fig. S6 (fourth column for D5L2A1)), suggesting narrow charge conjugation. The atomic indices (excluding hydrogen) for D5L2A3 in its three parts are as follows: (i) in donor are from 0 to 18, (ii) in π -spacer from 19 to 25 and (iii) in acceptor from 26 to 37. In D5L2A3 we observe very few variations in structural parameters showing less effects when in excited and cationic state (see SI Fig. S3(d) for bond lengths, SI Fig. S4(e) for bonds angles, SI Fig. S5(e) for dihedral angles and values in SI Table. S7 and SI Fig. S6(sixth column for D5L2A3)). Absence of any fused structures in D5L2A1 and D5L2A3 dyes might also contribute to the less efficient charge transfer.

4 Summary and Conclusion

The ground state geometry for selection of experimentally synthesized dye molecules ADEKA1, C275, C257, D5L2A1, CB4 and D5L2A3 is optimized using DFT. The UV-Vis spectra and bandgap computed using the ground state geometry and TDDFT method are found to be in reasonable match with the reported experimental results (see SI Fig. S1). Our charge density difference plots for excited states computed using TDDFT highlight different response of dyes. While dyes like ADEKA1, C275, D5L2A1, CB4 and D5L2A3 show effective charge separation and transfer from donor to acceptor (see Fig. 2 for first strong excited state and SI Fig. S2 for other excitation states), for C257 the charge appears to be localized on the donor instead of the acceptor group. Hence, our results for charge density difference maps capture the charge redistribution for different excitation states at a reasonable computational cost. The estimated electron and hole reorganization energy (λ) suggests that ADEKA1

Fig. 4 Change in the distance between the donor and acceptor group of ADEKA1 in ground state, excited state and cationic state. On removal of electron (cationic state) ADEKA1 shows highly planar acceptor group (blue highlighted box).

and C275 possess better electron and hole transfer abilities than other dyes. Additionally, these two dyes show significant increase in dipole moment (>2 Debye in going from ground to excited state), which is consistent with their reported high efficiency.

Further analysis based on the comparison and difference in the structural parameters of the dyes (i) between ground and excited, and (ii) between ground and cationic state, guided us to establish a more general correspondence between the molecular structural parameters, calculated electronic properties and resulting efficiency of the dyes. Additionally, the presence of fused structures only as donor in ADEKA1 and C275, as only π -spacer in CB4 has been observed to play an important role in supporting the understanding of ICT through structural changes. This study also finds that presence of fused structure as donor group results in smaller difference between the hole and electron recombination energy. Presence of fused structure only as π -spacer in D- π -A is observed to lower the electron recombination energy however, this is not yet conclusive and further study in this topic could be of interest for reader. Analysing the performance of the dye solely based on the recombination energy or the dipole moment are not conclusive and hence, structural analysis of dyes in various excited and ionic states helps to understand the ICT more effectively. The dyes like ADEKA1 (Fig. 4), C275 and C257 (SI Fig. S6) show prominent changes in the structural parameters in donor, and acceptor region, in both excited and cationic states. On the other hand, D5L2A1 demonstrate changes in π -spacer and in donor group respectively. However, no significant structural parameters changes were observed for D5L2A3.

Interestingly, we observe that efficient dyes show extended charge transfer, with higher possibility of charge migration over the molecular skeleton. The extent of charge transfer is directly related to the electron donating capacity of donor, and withdrawal capacity π -spacer and/or acceptor groups, extent of conjugation length and associated structural rearrangement of the groups. Our study of detailed structural modifications in photo-

excited dye molecules and associated loss of electron, accompanied by the calculation of resulting electron and hole reorganization energy reasonably explains why certain dye molecules show high photo-conversion efficiency in comparison to others and can assist in improving the design of the dyes for DSSCs. While we selected certain dye molecules as prototype, our approach proves to be simple yet significant for any dye molecule, to indeed aid the experimentalists to pre-estimate/manipulate the charge transfer process in such molecules, which in general has critical role in physics, chemistry, biology and material science.

Acknowledgements

ELI-ALPS is supported by the European Union and co-financed by the European Regional Development Fund (GI-NOP-2.3.6-15-2015-00001). KC and MUK acknowledge Project no. 2019-2.1.13-TÉT-IN-2020-00059 which has been implemented with the support provided from the National Research, Development and Innovation Fund of Hungary, financed under the 2019-2.1.13-TÉT-IN funding scheme.

Notes and references

- 1 B. O'regan and M. Grätzel, *nature*, 1991, **353**, 737–740.
- 2 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chemical reviews*, 2010, **110**, 6595–6663.
- 3 M. Ye, X. Wen, M. Wang, J. Iocozzia, N. Zhang, C. Lin and Z. Lin, *Materials Today*, 2015, **18**, 155–162.
- 4 S.-S. Sun, *Solar energy materials and solar cells*, 2003, **79**, 257–264.
- 5 F. Bella and C. Gerbaldi, *Encyclopedia of Polymer Science and Technology*, 2002, 1–17.
- 6 M. Freitag and G. Boschloo, *Current Opinion in Electrochemistry*, 2017, **2**, 111–119.
- 7 W. Ying, J. Yang, M. Wielopolski, T. Moehl, J.-E. Moser, P. Comte, J. Hua, S. M. Zakeeruddin, H. Tian and M. Grätzel, *Chemical Science*, 2014, **5**, 206–214.
- 8 B. S. Arslan, E. Güzel, T. Kaya, V. Durmaz, M. Keskin, D. Avcı,

- M. Nebioğlu and İ. Şişman, *Dyes and Pigments*, 2019, **164**, 188–197.
- 9 H. Zhou, J.-M. Ji, M. S. Kim and H. K. Kim, *Nanomaterials*, 2018, **8**, 1030.
- 10 J. Maçaira, L. Andrade and A. Mendes, *Renewable and Sustainable Energy Reviews*, 2013, **27**, 334–349.
- 11 C. C. Raj and R. Prasanth, *Journal of Power Sources*, 2016, **317**, 120–132.
- 12 J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan and G. Luo, *Chemical reviews*, 2015, **115**, 2136–2173.
- 13 B. Sebo, N. Huang, Y. Liu, Q. Tai, L. Liang, H. Hu, S. Xu and X.-Z. Zhao, *Electrochimica Acta*, 2013, **112**, 458–464.
- 14 M. Wu and T. Ma, *ChemSusChem*, 2012, **5**, 1343–1357.
- 15 K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-i. Fujisawa and M. Hanaya, *Chemical communications*, 2015, **51**, 15894–15897.
- 16 S. Caramori, V. Cristino, R. Boaretto, R. Argazzi, C. A. Bignozzi and A. Di Carlo, *International Journal of Photoenergy*, 2010, **2010**,.
- 17 J. N. Clifford, E. Martínez-Ferrero, A. Viterisi and E. Palomares, *Chemical Society Reviews*, 2011, **40**, 1635–1646.
- 18 S. Shalini, R. Balasundaraprabhu, T. S. Kumar, N. Prabhavathy, S. Senthilarasu and S. Prasanna, *International Journal of Energy Research*, 2016, **40**, 1303–1320.
- 19 R. Misra, R. Maragani, D. Arora, A. Sharma and G. D. Sharma, *Dyes and Pigments*, 2016, **126**, 38–45.
- 20 Y. Wang, B. Chen, W. Wu, X. Li, W. Zhu, H. Tian and Y. Xie, *Angewandte Chemie*, 2014, **126**, 10955–10959.
- 21 L. Zhang, X. Yang, W. Wang, G. G. Gurzadyan, J. Li, X. Li, J. An, Z. Yu, H. Wang, B. Cai *et al.*, *ACS Energy Letters*, 2019, **4**, 943–951.
- 22 Y. Gao, W. Guan and L. Yan, *The Journal of Physical Chemistry A*, 2018, **122**, 7491–7496.
- 23 C. Chitpakdee, S. Namuangruk, K. Suttisintong, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk, K. Sirithip, V. Promarak and N. Kungwan, *Dyes and Pigments*, 2015, **118**, 64–75.
- 24 K. Kakiage, Y. Aoyama, T. Yano, T. Otsuka, T. Kyomen, M. Unno and M. Hanaya, *Chemical Communications*, 2014, **50**, 6379–6381.
- 25 J.-i. Fujisawa, A. Osawa and M. Hanaya, *Physical Chemistry Chemical Physics*, 2016, **18**, 22244–22253.
- 26 C.-J. Chen, J. Zhang, Z.-H. Fu, H.-C. Zhu, H. Li and X.-F. Zhu, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2019, **222**, 117217.
- 27 Z.-J. Li, X.-H. Wang, W.-L. Tian, T.-Q. Huang, A.-L. Meng and L.-N. Yang, *Materials Today Communications*, 2020, **22**, 100839.
- 28 M. Zhang, L. Yang, C. Yan, W. Ma and P. Wang, *Physical Chemistry Chemical Physics*, 2014, **16**, 20578–20585.
- 29 M. Zhang, Y. Wang, M. Xu, W. Ma, R. Li and P. Wang, *Energy & Environmental Science*, 2013, **6**, 2944–2949.
- 30 J. Liang, C. Zhu and Z. Cao, *Physical Chemistry Chemical Physics*, 2013, **15**, 13844–13851.
- 31 D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, *Chemical Communications*, 2006, 2245–2247.
- 32 J. Liao, H. Zhao, Y. Xu, W. Zhou, F. Peng, Y. Wang and Y. Fang, *RSC Advances*, 2017, **7**, 33975–33985.
- 33 S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nature chemistry*, 2014, **6**, 242.
- 34 Z. Xu, S. Gao, X. Lu, Y. Li, Y. Li and S. Wei, *Physical Chemistry Chemical Physics*, 2020, **22**, 14846–14856.
- 35 S. Chen, Z. Pang and W. Wu, *International Journal of Energy Research*, 2020.
- 36 N. Wazzan and A. Irfan, *Materials Science in Semiconductor Processing*, 2020, **120**, 105260.
- 37 K. Pei, Y. Wu, A. Islam, S. Zhu, L. Han, Z. Geng and W. Zhu, *The Journal of Physical Chemistry C*, 2014, **118**, 16552–16561.
- 38 J. Zhang, Y.-H. Kan, H.-B. Li, Y. Geng, Y. Wu and Z.-M. Su, *Dyes and Pigments*, 2012, **95**, 313–321.
- 39 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *Journal of the American Chemical Society*, 1993, **115**, 6382–6390.
- 40 T. P. Chou, Q. Zhang, G. E. Fryxell and G. Cao, *Advanced Materials*, 2007, **19**, 2588–2592.
- 41 Y. Ooyama, S. Inoue, T. Nagano, K. Kushimoto, J. Ohshita, I. Imae, K. Komaguchi and Y. Harima, *Angewandte Chemie International Edition*, 2011, **50**, 7429–7433.
- 42 T. Leijtens, I.-K. Ding, T. Giovenzana, J. T. Bloking, M. D. McGehee and A. Sellinger, *ACS nano*, 2012, **6**, 1455–1462.
- 43 H. Li, K. Fu, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar and A. C. Grimsdale, *Angewandte Chemie International Edition*, 2014, **53**, 4085–4088.
- 44 J. Wu, P. Li, S. Hao, H. Yang and Z. Lan, *Electrochimica Acta*, 2007, **52**, 5334–5338.
- 45 S. Venkatesan, I.-P. Liu, J.-C. Lin, M.-H. Tsai, H. Teng and Y.-L. Lee, *Journal of Materials Chemistry A*, 2018, **6**, 10085–10094.
- 46 S. Ameen, M. S. Akhtar, M. Song and H. S. Shin, *ACS applied materials & interfaces*, 2012, **4**, 4405–4412.
- 47 G. Cheng, M. S. Akhtar, O.-B. Yang and F. J. Stadler, *ACS Applied Materials & Interfaces*, 2013, **5**, 6635–6642.
- 48 F. Ambrosio, N. Martsinovich and A. Troisi, *The Journal of Physical Chemistry Letters*, 2012, **Vol.3**, 1531–1535.
- 49 D. Jacquemin, V. Wathelet, E. A. Perpète and C. Adamo, *Journal of Chemical Theory and Computation*, 2009, **5**, 2420–2435.
- 50 N. Martsinovich and A. Troisi, *The Journal of Physical Chemistry C*, 2011, **115**, 11781–11792.
- 51 F. Schiffrmann, J. VandeVondele, J. Hutter, R. Wirz, A. Urakawa and A. Baiker, *The Journal of Physical Chemistry C*, 2010, **114**, 8398–8404.
- 52 Y. Jin, J.-A. Qiao, C. Liu, L. Luo, X. Chi, Y. Zhang and M.-H. Zeng, *The Journal of Physical Chemistry C*, 2019, **123**, 20093–20104.
- 53 Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chemical reviews*, 2003, **103**, 3899–4032.
- 54 Z. R. Grabowski and J. Dobkowski, *Pure and Applied Chemistry*, 1983, **55**, 245–252.
- 55 X. Jiang, J. Wang, W. Wang, Y. Yang, X. Zhan and X. Chen, *Dyes and Pigments*, 2019, **166**, 381–389.
- 56 C. Jia, S.-X. Liu, C. Tanner, C. Leiggener, A. Neels, L. Sanguinet, E. Levillain, S. Leutwyler, A. Hauser and S. Decurtins, *Chemistry—A European Journal*, 2007, **13**, 3804–3812.
- 57 C. M. Amb, S. Chen, K. R. Graham, J. Subbiah, C. E. Small, F. So and J. R. Reynolds, *Journal of the American Chemical Society*, 2011, **133**, 10062–10065.

- 58 R. Duan, G. Han, L.-B. Qu and Y. Yi, *Materials Chemistry Frontiers*, 2021.
- 59 Y. Wu, M. Marszalek, S. M. Zakeeruddin, Q. Zhang, H. Tian, M. Grätzel and W. Zhu, *Energy & Environmental Science*, 2012, **5**, 8261–8272.
- 60 M. C. Sil, L.-S. Chen, C.-W. Lai, C.-C. Chang and C.-M. Chen, *Journal of Materials Chemistry C*, 2020, **8**, 11407–11416.
- 61 M. A. Marques and E. K. Gross, *Annu. Rev. Phys. Chem.*, 2004, **55**, 427–455.
- 62 F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2012, **2**, 73–78.
- 63 F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2018, **8**, e1327.
- 64 M. Robb, J. Cheeseman and G. Scalmani, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
- 65 F. Weigend and R. Ahlrichs, *Physical Chemistry Chemical Physics*, 2005, **7**, 3297–3305.
- 66 F. Weigend, *Physical chemistry chemical physics*, 2006, **8**, 1057–1065.
- 67 A. Irfan and A. G. Al-Sehemi, *Journal of Saudi Chemical Society*, 2015, **19**, 318–321.
- 68 X. Xu and D. G. Truhlar, *Journal of chemical theory and computation*, 2011, **7**, 2766–2779.
- 69 Y. Takano and K. Houk, *Journal of Chemical Theory and Computation*, 2005, **1**, 70–77.
- 70 G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai et al., *Journal of the American Chemical Society*, 2005, **127**, 6335–6346.
- 71 R. Marcus, *The Journal of Chemical Physics*, 1956, **24**, 966–978.
- 72 R. Marcus, *Annu. Rev. Phys. Chem.*, 1964, 155–196.
- 73 R. Marcus, *Pure and Applied Chemistry*, 1997, **69**, 13–29.
- 74 J. Jortner, *The Journal of Chemical Physics*, 1976, **64**, 4860–4867.
- 75 M. Bixon and J. Jortner, *Advances in Chemical Physics*, 1999, **106**, 35–202.
- 76 N. Kestner, J. Logan and J. Jortner, *Journal of Physical Chemistry*, 1974, **78**, 2148–2166.
- 77 A. A. Kletsov, *Chemical Physics Letters*, 2014, **612**, 203 – 208.
- 78 D. Cahen, G. Hodes, M. Graetzel, J. F. Guillemoles and I. Riess, *The Journal of Physical Chemistry B*, 2000, **104**, 2053–2059.
- 79 J. B. Asbury, Y.-Q. Wang, E. Hao, H. N. Ghosh and T. Lian, *Research on Chemical Intermediates*, 2001, **27**, 393–406.
- 80 M. Blanchard-Desce, R. Wortmann, S. Lebus, J.-M. Lehn and P. Krämer, *Chemical physics letters*, 1995, **243**, 526–532.
- 81 J. Hu, Y. Li, H. Zhu, S. Qiu, G. He, X. Zhu and A. Xia, *ChemPhysChem*, 2015, **16**, 2357–2365.
- 82 S.-L. Wang and T.-I. Ho, *Journal of Photochemistry and photobiology A: Chemistry*, 2000, **135**, 119–126.
- 83 W. Ma, Y. Jiao and S. Meng, *Physical Chemistry Chemical Physics*, 2013, **15**, 17187–17194.
- 84 K. Kise, Y. Hong, N. Fukui, D. Shimizu, D. Kim and A. Osuka, *Chemistry–A European Journal*, 2018, **24**, 8306–8310.
- 85 H. Naito, K. Nishino, Y. Morisaki, K. Tanaka and Y. Chujo, *Angewandte Chemie International Edition*, 2017, **56**, 254–259.
- 86 S. Karmakar, A. Ambastha, A. Jha, A. K. Dharmadhikari, J. A. Dharmadhikari, R. Venkatramani and J. Dasgupta, *The Journal of Physical Chemistry Letters*, 2020.
- 87 Y. Liu, X. Zhang, C. Li, Y. Tian, F. Zhang, Y. Wang, W. Wu and B. Liu, *The Journal of Physical Chemistry C*, 2019, **123**, 13531–13537.
- 88 Z.-Z. Sun, X.-J. Geng, W.-L. Ding, S. Feng, Y.-L. Xu, Y.-L. Li, Z.-Y. Xiao, S.-J. Sun, Z.-Q. Zhao and J.-F. Liu, *Synthetic Metals*, 2018, **237**, 1–9.

Supplementary Information

Fig. S1 UV-VIS absorption TDDFT spectra calculated for (a) ADEKA1, (b) C275, (c) C257, (d) CB4, (e) D5L2A1 and (f) D5L2A3; is plot with Gaussian broadening of full width half maxima (FWHM) of 10 nm.

Fig. S2 Charge density difference maps for (a) ADEKA1, (b) C275, (c) C257, (d) CB4, (e) D5L2A1 and (f) D5L2A3 in different excited states. The purple colour show decrease in electron density and yellow colour show the increase in electron density. [Atoms (colour): C (cyan), N (blue), O (red), S (yellow), H (gray), B (pink), Si (dark yellow)]

Species	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV) (reference)	(S_0) (debye)	(S_n) (debye)
ADEKA1	-5.41	-2.68	2.73 (*1.85 ²⁴)	12.24	(S_1) 14.26
C275	-5.20	-2.80	2.40 (*2.07 ⁸⁸)	5.76	(S_1) 7.91
C257	-5.18	-2.59	2.59 (*1.86 ²⁹)	6.43	(S_3) 3.60
D5L2A1	-5.48	-2.93	2.55 (*2.42 ³⁰)	10.32	(S_2) 7.72
CB4	-5.99	-2.88	3.11 (*1.92 ³²)	6.39	—
D5L2A3	-5.46	-2.94	2.52 (*2.18 ³⁰)	7.62	(S_2) 8.27

Table S1 Energy of HOMO, LUMO, Energy gaps (*reference value), ground state dipole moment (S_0) and ground state dipole moment in excited state (S_n). For CB4 geometry optimization did not converge for sixth excited state.

Fig. S3 Variations in bond length for (a) C275, (b) C257, (c) D5L2A1 and (d) D5L2A3; between ground state and excited state (red) and ground state and cationic state (blue). *for $\Delta > 0.02\text{\AA}$.

Fig. S4 Variations in bond angle for (a) ADEKA1, (b) C275, (c) C257, (d) D5L2A1 and (e) D5L2A3; between ground state and excited state (red) and ground state and cationic state (blue). *for $\Delta > 2^\circ$.

Fig. S5 Variations in dihedral angle for (a) ADEKA1, (b) C275, (c) C257, (d) D5L2A1 and (e) D5L2A3; between ground state and excited state (red) and ground state and cationic state (blue). *for $\Delta > 40^\circ$.

Fig. S6 Change in the distance between the donor and acceptor group of dye molecules in ground state, excited state and cationic state. red box for donor, green box for π -spacer and blue box for acceptor highlights the planar behaviour in dye when in excited and cationic state.

Dye	λ in nm (Excited state)	Molecular orbital contribution	OS	τ (ns)
ADEKA1	643.5 (1)	$HOMO \rightarrow LUMO$ (97%)	0.75	8.27
	450.2 (2)	$HOMO - 1 \rightarrow LUMO$ (84.39%) $HOMO \rightarrow LUMO + 1$ (11.10%)	0.91	3.33
	419 (3)	$HOMO - 2 \rightarrow LUMO$ (47.79%) $HOMO \rightarrow LUMO + 2$ (36.37%)	0.28	9.41
	386.5 (4)	$HOMO \rightarrow LUMO + 1$ (37.36%) $HOMO - 4 \rightarrow LUMO$ (29.42%)	0.35	6.39
	373.7 (6)	$HOMO - 2 \rightarrow LUMO$ (26.41%) $HOMO - 3 \rightarrow LUMO$ (44.57%) $HOMO - 4 \rightarrow LUMO$ (38.13%)	0.12	17.4
C275	808.5 (1)	$HOMO \rightarrow LUMO$ (97.87%)	0.556	17.619
	463.1 (2)	$HOMO \rightarrow LUMO + 1$ (91.32%)	0.851	3.77
	391 (6)	$HOMO - 3 \rightarrow LUMO$ (82.42%)	0.21	10.61
C257	671.5 (3)	$HOMO \rightarrow LUMO$ (97.05%)	0.8	8.37
	541 (5)	$HOMO - 1 \rightarrow LUMO$ (92.42%)	0.08	50.4
	483.4 (6)	$HOMO \rightarrow LUMO + 1$ (90.46%)	0.70	4.96
D5L2A1	667.8 (2)	$HOMO - 1 \rightarrow LUMO + 1$ (96.96%)	0.99	6.76
	386.4 (5)	$HOMO - 1 \rightarrow LUMO$ (41.22%) $HOMO \rightarrow LUMO + 1$ (15.36%)	0.85	2.62
CB4	497.3 (6)	$HOMO - 1 \rightarrow LUMO$ (54.28%) $HOMO \rightarrow LUMO$ (25.78%)	0.65	5.62
		$HOMO - 2 \rightarrow LUMO$ (14.22%)		
	405.3 (8)	$HOMO - 2 \rightarrow LUMO$ (77.10%)	0.74	3.31
D5L2A3	719.6 (2)	$HOMO \rightarrow LUMO$ (97.19%)	0.71	10.8
	427.4 (6)	$HOMO - 1 \rightarrow LUMO$ (89.43%)	0.91	2.99

Table S2 Calculated the excitation lifetime τ (ns), molecular orbital contribution for the excitation states with high oscillator (OS) strength for ADEKA1, C275, C257, CB4, D5L2A1 and D5L2A3.

Definition	ΔE	Definition	ΔC
B(C14,N13)	-0.0119	B(C16,C14)	-0.0124
B(C16,C14)	-0.0244	B(C19,C16)	0.0263
B(C19,C16)	0.0311	B(C20,C19)	0.0318
B(C20,C19)	0.0142	B(C22,S21)	0.0272
B(C22,S21)	0.0244	B(C23,C22)	0.0274
B(C23,C22)	0.0268	B(C27,C22)	0.0393
B(C24,C20)	-0.0307	B(C28,C27)	-0.0156
B(C24,C23)	0.0244	B(C29,C28)	-0.0183
B(C28,C27)	-0.043	B(C30,C29)	-0.0348
B(C29,C28)	0.0199	B(C34,C30)	-0.0245
B(C30,C29)	-0.0208	B(C36,S35)	0.0112
B(C34,C30)	0.0196	B(C37,C36)	0.0181
B(C36,S35)	0.0114	B(C38,C34)	-0.033
B(C38,C34)	-0.0426	B(C38,C37)	-0.0311
B(C41,C36)	-0.024	B(C41,C36)	0.0103
B(C44,C43)	0.0208	B(C42,C41)	0.0156
B(C48,C44)	0.0266	B(C43,C42)	-0.0124
B(C50,C49)	0.0122	B(C44,C43)	0.0141
B(S31,C27)	-0.0202	B(N13,C2)	-0.0114
B(S31,C30)	0.0162	B(N55,C51)	0.017
B(Si6,C5)	0.013	B(S31,C30)	0.029
nan	NaN	B(S35,C34)	0.0175
nan	NaN	B(Si6,C5)	0.0132
A(C14,C16,C17)	3.19	A(C14,C16,C17)	2.76
A(C14,C16,C19)	-3.12	A(C14,C16,C19)	-3.08
A(C23,C24,C25)	-2.62	A(C16,C19,C20)	-2.82
A(C30,C34,S35)	2.98	A(C20,C24,C25)	2.99
A(C37,C36,C41)	-6.09	A(C34,C38,C39)	-3.34
A(C37,C38,C39)	-2.96	A(C36,C41,S45)	3.12
A(C38,C39,C40)	-2.67	A(C37,C36,C41)	-4
A(S35,C36,C41)	-6.2	A(C37,C38,C39)	-3.12
		A(Si6,O7,C8)	-2.74
D(C8,O7,Si6,O9)	20.34	D(C12,O11,Si6,C5)	-25.41
D(C8,O7,Si6,O11)	22.14	D(C12,O11,Si6,O7)	24.85
D(C17,C16,C14,N13)	-20.39	D(C38,C34,C30,C29)	124.34
D(C26,C25,C24,C20)	92.22	D(C38,C34,C30,S31)	59.92
D(C26,C25,C24,C23)	-86.23	D(C40,C39,C38,C34)	48.74
D(C38,C34,C30,C29)	123.29	D(C40,C39,C38,C37)	-21.99
D(C38,C34,C30,S31)	-27.14	D(C42,C41,C36,C37)	-28.17
D(C40,C39,C38,C34)	50.45	D(C49,C48,C44,C43)	-93.96
D(C42,C41,C36,C37)	-12.28	D(C49,C48,C44,S45)	-62.86
		D(H79,C25,C24,C20)	-63.83
D(H68,C8,O7,Si6)	20.54	D(H91,C39,C38,C34)	36.82
D(H74,C12,O11,Si6)	-22.71	D(H91,C39,C38,C37)	-44.39
D(H75,C12,O11,Si6)	25.86	D(H92,C39,C38,C34)	-33.69
D(H79,C25,C24,C23)	97.68	D(H92,C39,C38,C37)	-38.65
D(H80,C25,C24,C20)	22.72	D(O7,Si6,C5,C0)	42.56
D(H91,C39,C38,C34)	-50.73	D(O9,Si6,C5,C0)	23.07
D(H92,C39,C38,C34)	24.38	D(O9,Si6,C5,C4)	119.53
D(H92,C39,C38,C37)	-29.29	D(O11,Si6,C5,C0)	-25.23
D(O7,Si6,C5,C4)	-30.69	D(S35,C34,C30,C29)	-12.19
D(O11,Si6,C5,C4)	-42.21	D(S35,C34,C30,S31)	29.65
D(S35,C34,C30,C29)	-34.11		
D(S35,C34,C30,S31)	-29.77		

Table S3 Changes of bond length (B) in angstroms, bond angle (A) and dihedral angle (D) in degrees for ADEKA1 during relaxation from ground state to excited state (ΔE) and cationic state (ΔC). Change in bond length, bond angle or dihedral angle connecting donor and acceptor is highlighted by green box.

Definition	ΔE	Definition	ΔC
B(C5,C0)	0.0183	B(C2,C1)	0.0209
B(C6,C5)	0.0309	B(C6,C5)	0.0132
B(C8,C7)	-0.0117	B(C14,C12)	0.0171
B(C14,C12)	0.0138	B(C34,C27)	-0.0159
B(C27,C2)	-0.017	B(C37,C33)	-0.012
B(C34,C27)	-0.0172	B(C38,C32)	0.0129
B(C34,C33)	-0.0157	B(C44,C37)	-0.0172
B(C37,C33)	-0.029	B(C45,C44)	-0.0155
B(C37,C36)	-0.0141	B(C46,C45)	0.0299
B(C38,C32)	0.0123	B(C49,C48)	-0.0344
B(C39,C38)	-0.0101	B(C50,C46)	-0.0347
B(C44,C37)	-0.032	B(C50,C49)	-0.025
B(C50,C49)	-0.0332	B(C55,C48)	0.0123
B(C60,C55)	0.0106	B(C61,C57)	-0.012
B(O28,C9)	-0.0195	B(N53,S52)	-0.0154
nan	NaN	B(N54,S52)	-0.0204
nan	NaN	B(O28,C9)	-0.015
A(C0,C12,C13)	5.38	A(C0,C12,C13)	3.34
A(C0,C12,C14)	2.66	A(C12,C14,C24)	2.75
A(C12,C14,C23)	-3.26	A(C13,C12,C14)	-3.3
D(C14,C12,C11,C10)	-21.43	D(C13,C12,C11,C6)	22.16
D(C18,C13,C12,C11)	21.27	D(C17,C13,C12,C0)	21.71
D(C23,C14,C12,C11)	25.89	D(C17,C13,C12,C11)	24.84
D(C23,C14,C12,C13)	28.23	D(C18,C13,C12,C11)	20.06
D(C50,C46,C37,C36)	26.48	D(C23,C14,C12,C13)	37.39
D(C51,C46,C37,C36)	23.28	D(C24,C14,C12,C11)	-44.35
D(C60,C55,C48,C49)	20.09	D(C24,C14,C12,C13)	44.9
D(H77,C25,C15,C16)	69.53	D(C51,C46,C37,C33)	-24.48
D(H77,C25,C15,C19)	-48.8	D(C59,C55,C48,C47)	-21.76
D(H78,C25,C15,C16)	-68.63	D(C60,C55,C48,C47)	22.24
D(H78,C25,C15,C19)	-64.84	D(H78,C25,C15,C19)	-48.55
D(H79,C26,C21,C20)	20.69	D(H81,C26,C21,C22)	22.11
D(H79,C26,C21,C22)	-21.48	nan	NaN
D(H81,C26,C21,C20)	-23.57	nan	NaN

Table S4 Changes of bond length in angstroms, angle and dihedral angle in degrees for C275 during relaxation from ground state to excited state (ΔE) and cationic state (ΔC). Change in bond length, bond angle or dihedral angle connecting donor and acceptor is highlighted by green box.

Definition	ΔE	Definition	ΔC
B(C6,C4)	0.031	B(C17,C16)	-0.022
B(C7,C6)	0.02	B(C22,C21)	-0.02
B(C16,C15)	0.0248	B(C28,C26)	0.0261
B(C17,C16)	-0.0268	B(C31,N29)	0.0326
B(C23,C22)	0.0285	B(C49,C0)	0.0276
B(C30,N29)	0.0292	B(N29,C28)	-0.0254
B(N29,C28)	-0.0636		
B(O43,C39)	-0.0202		
B(S52,C6)	-0.021		
A(N29,C30,C32)	2.55	A(C4,C6,C7)	3.11
		A(C4,C6,S52)	3.59
		A(C20,C22,C23)	-3.4
		A(C26,C28,C27)	-2.73
		A(C28,N29,C30)	-3.32
		A(C28,N29,C31)	4.71
		A(C30,N29,C31)	-6.15
		A(O50,C49,O51)	-2.51
D(C7,C6,C4,C3)	34.43	D(C7,C6,C4,C3)	32.01
D(C18,C17,C16,C15)	20.54	D(C7,C6,C4,C5)	36.05
D(C25,C23,C22,C20)	20.71	D(C18,C17,C16,S53)	21.21
D(C31,N29,C28,C27)	-46.22	D(C19,C17,C16,S53)	21.46
D(C32,C30,N29,C28)	21.31	D(C30,N29,C28,C26)	48.5
D(C33,C30,N29,C28)	23.56	D(C30,N29,C28,C27)	-49.1
D(C33,C30,N29,C31)	-22.83	D(C31,N29,C28,C26)	-45.61
D(S52,C6,C4,C3)	-24.42	D(C31,N29,C28,C27)	-44.4
		D(C41,C31,N29,C28)	29.2
		D(C41,C31,N29,C30)	-25.42
		D(S52,C6,C4,C3)	-33.74

Table S5 Changes of bond length in angstroms, angle and dihedral angle in degrees for C257 during relaxation from ground state to excited state (ΔE) and cationic state (ΔC). Change in bond length, bond angle or dihedral angle connecting donor and acceptor is highlighted by green box.

Definition	ΔE	Definition	ΔC
B(C13,N6)	-0.0388	B(C10,N6)	0.0262
B(C19,C2)	0.0241	B(C13,N6)	-0.0336
B(C24,C23)	-0.0207	B(C26,C24)	0.0267
B(C28,C27)	0.0208	B(C27,C26)	-0.0366
B(N6,C5)	0.0793	B(N6,C5)	0.0508
		B(S25,C24)	-0.0221
A(C10,N6,C13)	-4.99	A(C5,N6,C10)	3.95
D(C11,C10,C9,C8)	-46.92	D(C10,N6,C5,C4)	-46.49
D(C13,N6,C5,C4)	47.72	D(C11,C10,C9,C8)	-49.9
D(C14,C13,N6,C5)	47.7	D(C14,C13,N6,C5)	43.77
D(C14,C13,N6,C10)	-27.91	D(C15,C14,C13,C18)	30.97
D(C18,C17,C16,C15)	-34.81	D(C18,C13,N6,C10)	31.09

Table S6 Changes of bond length in angstroms, angle and dihedral angle in degrees for D5L2A1 during relaxation from ground state to excited state (ΔE) and cationic state (ΔC). Change in bond length, bond angle or dihedral angle connecting donor and π -spacer is highlighted by blue box and connecting structural parameters between π -spacer and acceptor is highlighted by red box.

Definition	ΔE	Definition	ΔC
B(C5,C4)	-0.0205	B(C19,C2)	0.0233
B(C10,N6)	0.0233	B(C29,S27)	0.0226
B(C13,N6)	0.029	B(C34,C24)	0.029
B(C21,C20)	0.0273	B(N6,C5)	0.0558
B(C28,C26)	0.0428		
B(C29,S27)	0.0292		
B(C34,C26)	-0.0361		
A(C10,N6,C13)	-3.2	A(C23,C24,C34)	-3.34
A(C23,C24,C34)	-2.59	A(C28,C26,C34)	-2.57
A(C28,C26,C34)	-2.82	A(S27,C26,C34)	2.79
A(S27,C26,C34)	2.88		

Table S7 Changes of bond length in angstroms, angle and dihedral angle in degrees for D5L2A3 during relaxation from ground state to excited state (ΔE) and cationic state (ΔC). Change in bond length, bond angle or dihedral angle connecting donor and π -spacer is highlighted by blue box and connecting structural parameters between π -spacer and acceptor is highlighted by red box.