Novel Dyes Design Based on First Principles and the Prediction of Energy Conversion Efficiencies of Dye-Sensitized Solar Cells

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ABSTRACT: With the depletion of fossil energy, solar energy has gradually attracted people’s attention. Dye-sensitized solar cells have developed rapidly in recent years due to their low cost and high conversion efficiency. In this article, based on the theoretical research on the photovoltaic parameters of DSSCs in the early stages of the research team, we have made an accurate prediction of $J_{sc}$, $V_{oc}$, and PCE of C286. (The error in our predicted PCE values was 3.33% relative to the experiment.) Also, we further designed a series of new dyes CH1–CH5 by introducing donors and co-acceptors with C286–C288 as the prototype using the DFT/TDDFT method. The PCE of the designed dyes CH2–CH5 exceed the given dye C286, especially the CH3 and CH4 obtained the PCE of 26.2 and 14.5%. This indicates the proposed dyes offer a dramatic improvement on PCE for DSSC devices. Moreover, the designed dyes such as CH3 and CH4 have great potential to be applied to photovoltaic applications, further enabling the design of novel, highly efficient photoactive materials.

INTRODUCTION

With the increase of population and the exhaustion of nonrenewable energy, sustainable energy is one of the most pressing issues. Renewable energy includes geothermal, wind, and solar energy, of which solar energy is the most abundant and easiest to use. The development and utilization of solar energy are an effective means to solve the energy shortage problem. Silicon solar cells are the earliest commercial solar cells to be developed. Due to its series of shortcomings, it has gradually attracted people’s attention. Dye-sensitized solar cells have a photoelectric conversion efficiency (PCE) of 7.1%, it quickly became the focus of scientific research and achieved a quick development. Wang Peng and his team synthesized other pure organic dye molecules C281 (the specific molecular schematic of C281 is shown in Figure S1†) having a photoelectric conversion efficiency of 13.1%; its efficiency exceeded that of metal complex dyes.

Traditionally, DSSCs have been the mainstream of organometallic dyes. Because of their low cost and sufficient availability, organometallic dyes are increasingly replaced by organic metal-free dyes due to their versatile molecular design. Natural dyes open the door to alternative synthetic sensitizers because of their low cost and nontoxic advantages, but the efficiency of natural dyes is not up to standard. Mainly due to the photodegradation of natural materials in sunlight, the light is degraded, making it very inefficient. Ultimately, researchers have focused on organic nonmetallic dyes.

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At present, organic metal-free dyes can be divided into indole dyes, coumarin dyes, semi-anthocyanin dyes, polyenes dyes, and triphenylamine dyes. Triphenylamine dyes are one of the most common dyes currently used, with good optical properties. The design of these dyes is based on the simplest structure of electron donor (D), \( \pi \)-conjugate bridge (\( \pi \)), and electron receptor (A). This electron donor–\( \pi \)-receptor (D–\( \pi \)-A) structure directly binds the receptor directly to the surface of an organic metal-free dye semiconductor. This will facilitate the rapid transfer of the electron from the excited state of the dye to the semiconductor band and the return of the dye from the excited state to the ground state through the redox process, which is semiconductor band and the return of the dye from the excited state to the ground state through the redox process. This also shows that the \( \pi \)-A coplanar can obtain better battery performance in some conditions. They also indicated that dye molecules can obtain better DSSC performance without having higher homo energy levels.

We studied their design ideas and tried to devise more efficient D–\( \pi \)-A organic dyes. We first designed and screened the second donor and \( \pi \)-conjugated bridge and further designed a batch of precursor dyes for this purpose. In the next step, the selected second donor and \( \pi \)-conjugated bridge formed a novel organic dye; these novel dyes were used to construct DSSC structural models and to perform photovoltaic performance calculations and characterization.

We consider that the second donor and \( \pi \)-conjugated bridges are the key factors affecting the properties of the dyes and their DSSC in the novel type D–\( \pi \)-A organic dyes. For this purpose, we first designed a batch of precursor dyes to help us select the second donor and the \( \pi \)-conjugated bridge. The molecular structure diagram of the designed precursor dyes is shown in Figure S2-3, where C286g is the reference dye, and it is the simplified model of C286 in Figure 1. This simplified model mainly removes the alkyl branches on the basis of the original dye molecules, and the branches have little effect on the spectral performance, so this simplified model can be used to reduce the calculation time.

We can see from Figure S4 that the dyes C860g and C862g, which have high molar extinction coefficient and deep discoloration absorption, have a bright prospect of adsorption on the surface of TiO2 and can greatly increase the \( J_c \) value, thereby improving the PCE of DSSC. Based on the above experience, a series of novel organic dyes have been designed by the orthogonal method from the second donor and \( \pi \)-conjugated bridge (Figure 2).

\section*{Computational Details}

The calculation of all isolated dye molecules is done in Gaussian 09 software package; the chemical structure and excited states of organic dyes were studied using the first-principle density-functional theory (DFT) and time-dependent...
DFT (TDDFT) calculation. The geometric structure of the dyes was optimized by B3LYP and 6-31G(d) basis set. The solvent was the CPCM model and dichloromethane solvent. The excited states were calculated using CAM-B3LYP and 6-311G. The number of excited states was set to 10, and the solvent was still using the CPCM model and dichloromethane solvent.

The relevant quantum chemical simulations of the TiO₂ and TiO₂-dye composite systems are carried out by VSAP calculation using the DFT + U method. Since the system contains transition metal titanium atoms, the problem of defects in large-period metal elements can be compensated with +U. The parameter optimization method of the PEB exchange–correlation function in the generalized gradient approximation (GGA) method. The K-point sampling uses an automatic generation method centered on the γ point. We found that in the +U correction, when \( U = 6.0 \text{ eV} \) and \( J = 0.5 \text{ eV} \), the band gap, lattice parameter, and band gap value of TiO₂ are suitable.

### RESULTS AND DISCUSSION

After the novel dye structure model is constructed, the first-principle density-functional theory is used to calculate the necessary quantization of dyes and their sensitized DSSC, and then we process the results of the quantitative calculation to calculate the photovoltaic performance parameters of the novel DSSCs.

To obtain the adsorption density of dyes on the TiO₂ surface, we first assume that there is no agglomeration between dye molecules. The maximum density of the dye molecules adsorbed on the TiO₂ substrate was calculated, and the effect of this hypothesis was minimized by a correction factor. The calculated dye loading of CH₁–CH₅ under ideal conditions is 537.5/576.5/575.9/459.2/341.7 mmol/L, respectively. Here, the thickness of TiO₂ is 10 \( \mu \text{m} \), which is commonly used. This experimental value is still used in the subsequent calculations.

Chemical optimization of the electron-withdrawing groups should allow regulating the photoabsorption of the dyes. To understand the effect of heteroatoms in the acceptor group on the light-trapping efficiency, TDDFT was used to simulate the UV–vis absorption spectra of CH₁–CH₅ and C286g, which showed broad absorption spectra (Figure 3). From the absorption spectra of Figure 3, we can see that CH₃–CH₅ has a wide range of absorption spectra, while the absorption range of CH₁ and CH₂ is narrower, and the main absorption peak is located at the junction of the UV light region and the visible light region. Therefore, the absorbability of CH₁ and CH₂ is weak, and the absorbability of CH₃–CH₅ is stronger.

Figure 4 shows the light capture efficiency distribution curve of the five dyes. It is well known that the efficiency of the DSSC devices depends on \( J_{sc} – V_{oc} \) the filling factor (FF), and the incident solar cell (\( P_{inc} \)). Their relationship can be expressed as follows

\[
\eta = \frac{FF J_{sc} V_{oc}}{P_{inc}}
\]

There is a direct relationship between the efficiency of \( J_{sc} \) and DSSCs. The size of \( J_{sc} \) directly determines the efficiency of DSSCs. The main determinant of the size of \( J_{sc} \) is LHE, the short-circuit current density; \( J_{sc} \) can be defined as

\[
J_{sc} = \int LHE(\lambda) \Phi_{\text{inj}} \eta_{\text{reg}} \eta_{\text{coll}} d\lambda
\]

where \( \Phi_{\text{inj}} \) is the electron injection efficiency, \( \eta_{\text{reg}} \) is the dye regeneration efficiency, and \( \eta_{\text{coll}} \) is the charge collection efficiency.
efficiency. From the above equation, we can draw a conclusion that the level of LHE can affect the efficiency of DSSC.

For the convenience of observation, some images are amplified (as shown in the illustrations). It can be seen that CH1 and CH2 have strong absorption of the visible light in the range of 350–650 nm wavelength, but almost all CH3–CH5 have strong absorption in the range of 350–1100 nm. As we all know, DSSCs with high molar extinction coefficient and wide absorption range is the direction of the synthesis of new dyes.

The energy arrangement of the interface structure of dye-TiO2 relative to other components is an important parameter to determine how the properties of the DSSC working electrode affect the photovoltaic performance of the DSSC devices. Therefore, DFT and TDDFT are used to simulate the interface structure and energy arrangement. Figure 5 shows the partial density of state (PDOS) for the dye adsorption configurations of each dye-TiO2 interface. To facilitate the observation of important peaks, the data is logarithmically processed, so that we can easily find the peaks and valleys in the PDOS distribution curve of the dye. The HOMO level and the LOMO level of the dye are indicated by arrows (the extracted data are shown in Table 1). All dye-TiO2 models conformed to the mandatory energy alignment requirements for functional DSSC devices, that is, the luminescence of the dye must be above and overlapped with the minimum (CBM) edge of the conduction band of the TiO2 substrate. Thus, the excited dye can be effectively injected into the conductive band (CB) of TiO2.

Figure 6 shows the derivative diagram (PDOS-DER) of the partial wave state density map of TiO2 in each DSSC. An important energy level $E_{\text{FDD}}$ can be read from the position of the blue line mark (see Table 1 for the extracted data). We can find that all of the similar two sets of curves (herein referred to as double-wave curves) of all PDOS-DER maps are superimposed, and the peak positions corresponding to the double-wave curves are the same. Since the peak position of $E_{\text{FDD}}$ of some dye-sensitive molecules is not obvious, we can easily find $E_{\text{FDD}}$ in the obtained PDOS-DER by deriving its PDOS pattern. This is the first time that our research team has discovered and applied it to the DSSC’s theoretical efficiency prediction, and it has been perfectly verified by experiments.

The $I$–$V$ curves and $P$–$V$ curves of each DSSC are given in Figures 7 and 8, it was observed that different structure of donor changes the $I$–$V$ characteristics of the resulting DSSC to a great extent as can be seen in Figure 7. From the diagram, it can be seen that compared with the reference DSSC, C286g, the photovoltaic performance of CH1 is relatively poor, the difference between CH2 and CH5 is not large, and the photovoltaic performances of CH3 and CH4 are relatively better. The results calculated in Table 2 are also in agreement with the results shown in Figure 7. The redox potential of the

| Table 1. Key Energy Parameters (eV) of CH1–CH5 and C286g-Sensitized DSSCs |
|------------------|------------------|------------------|------------------|------------------|
|                 | HOMO             | LOMO             | $E_{\text{CBM}}$ | $E_{\text{FDD}}$ | $E_{\text{f}}$  |
| CH1              | -4.91            | -4.13            | -4.50            | -4.52            | -4.71           |
| CH2              | -4.76            | -4.05            | -4.48            | -4.50            | -4.62           |
| CH3              | -4.74            | -3.92            | -4.50            | -4.52            | -4.62           |
| CH4              | -4.70            | -4.21            | -4.51            | -4.53            | -4.61           |
| CH5              | -4.70            | -4.17            | -4.56            | -4.58            | -4.64           |
| C286g            | -4.81            | -3.72            | -4.52            | -4.52            | -4.66           |

Figure 5. PDOS of the dye (red) and TiO2 (black) in CH1–CH5 or C286g-sensitized DSSCs.
electrolyte solution used in the calculation of the correction factor is still $-5.02 \text{ eV}$.\textsuperscript{54–56}

This potential value has a better matching degree with the important energy-level parameters of the DSSCs calculated in Table 1. According to the results of the previous literature, it can be found that the potential of the electrolyte can be adjusted to a large extent by adjusting the concentration of electrolyte solution and the type of the electrolyte (including this value). On the basis of the results of the photovoltaic performance of the above DSSCs, we think that CH$_3$ and CH$_4$ and their derivatives are expected to be a novel organic dye to improve the photovoltaic performance of DSSCs, and CH$_3$ is probably the most promising one. The trends for the theoretical values should be consistent, and we expect the experimenters to use our conclusions to conduct relevant experimental investigations to verify our results.
CONCLUSIONS
To sum up, five novel organic dye molecules CH1–CH5 were designed based on π–A coplanar novel organic dye molecules C286, C287, and C288. The molecular structure models of five dye-sensitized DSSCs were constructed, and the important photovoltaic performance parameters of each DSSC were calculated using the novel calculation model. The results show that the CH3–CH4 dyes and their derivatives are expected to improve the photovoltaic performance of DSSCs, and CH3 presented as a particularly promising dye candidate to improve the core photovoltaic performance parameters of DSSCs. We expect relevant experimenters to use our conclusions to explore and validate our results.

ASSOCIATED CONTENT
Supporting Information
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Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Pullen, S.; Brinkert, K. SolEn for a Sustainable Future: Developing and Teaching a Multidisciplinary Course on Solar Energy To Further Sustainable Education in Chemistry. J. Chem. Educ. 2014, 91, 1569–1573.

(2) An, N.; Cai, Y.; Wu, H.; Tang, A.; Zhang, K.; Hao, X.; Ma, Z.; Guo, Q.; Ryu, H. S.; Woo, H. Y.; Sun, Y.; Zhou, E. Solution-Processed Organic Solar Cells with High Open-Circuit Voltage of 1.3 V and Low Non-Radiative Voltage Loss of 0.16 V. Adv. Mater. 2020, 32, No. 0002122.

(3) Tang, A.; Song, W.; Xiao, B.; Guo, J.; Min, J.; Ge, Z.; Zhang, J.; Wei, Z.; Zhou, E. Benzotriazole-Based Acceptor and Donors, Coupled with Chlorination, Achieve a High VOC of 1.24 V and an Efficiency of 10.5% in Fullerene-Free Organic Solar Cells. Chem. Mater. 2019, 31, 3941–3947.

(4) Tang, A.; Li, J.; Zhang, B.; Peng, J.; Zhou, E. Low-Bandgap n-Type Polymer Based on a Fused-DAD-Type Heptacyclic Ring for All-Polymer Solar Cell Application with a Power Conversion Efficiency of 10.7%. ACS Macro Lett. 2020, 9, 706–712.

(5) Cole, J. M.; Low, K. S.; Ozone, H.; Stathi, P.; Kitamura, C.; Kurata, H.; Rudolf, P.; Kawase, T. Data mining with molecular design rules identifies new class of dyes for dye-sensitised solar cells. Phys. Chem. Chem. Phys. 2014, 16, 26684–26690.

(6) Huang, J. H.; Lin, P. H.; Li, W. M.; Lee, K. M.; Liu, C. Y. Sn- and Pd-Free Synthesis of D−π−A Organic Sensitizers for Dye-Sensitized Solar Cells by Cu-Catalyzed Direct Arylation. ChemSusChem 2017, 10, 2284–2290.

(7) Jiao, Y.; Mao, L.; Liu, S.; Tan, T.; Wang, D.; Cao, D.; Mi, B.; Gao, Z.; Huang, W. Effects of meta or para connected organic dyes for dye-sensitized solar cell. Dyes Pigm. 2018, 158, 165–174.

(8) Jalali, T.; Arkian, P.; Golshani, M.; Jalali, M.; Osfouri, S. Performance evaluation of natural native dyes as photosensitizer in dye-sensitized solar cells. Opt. Mater. 2020, 110, No. 110441.

(9) Wang, Z.; Zang, X.-F.; Shen, H.; Shen, C.; Ye, X.; Li, Q.; Quan, Y.-Y.; Ye, F.; Huang, Z.-S. Dithienopyrrolobenzothiadiazole-based metal-free organic dyes with double anchors and thiophene spacers for efficient dye-sensitized solar cells. Sol. Energy 2020, 208, 1103–1113.

(10) Ren, Y.; Cao, Y.; Zhang, D.; Zakeeuddin, S. M.; Hagfeldt, A.; Wang, P.; Grätzel, M. A Blue Photosensitizer Realizing Efficient and Stable Green Solar Cells via Color Tuning by the Electrolyte. Adv. Mater. 2020, 32, No. 2000193.

(11) Xie, H. R.; Sun, D. Y.; Wei, Y. F.; Yuan, Y.; Zhang, J.; Ren, Y. T.; Wang, P. Thiencarbazolebenedrazole based organic dyes for transparent solar cells with over 10% efficiency. J. Mater. Chem. A 2019, 7, 11338–11346.

(12) Wu, H.; Zhang, J.; Ren, Y.; Zhang, Y.; Yuan, Y.; Shen, Z.; Li, S.; Wang, P. Tuning the Color Palette of Semi-Transparent Solar Cells via Lateral π-Extension of Polycyclic Heteroaromatics of Donor–Acceptor Dyes. ACS Appl. Energy Mater. 2020, 3, 4549–4558.

(13) Regan, B. O.; Grätzel, M.; Regan, B. O.; Grätzel, M.; Regan, B. O.; Grätzel, M.; Regan, B. O.; Grätzel, M. Synthesis of nanocrystalline titanium dioxide dye sensitised solar cell. Nature 1991, 353, 737–781.

(14) Wang, P.; Yao, Z.; Wu, H.; Li, Y.; Wang, J.; Zhang, J.; Zhang, M.; Guo, Y. Dithienopinacarbazole as the kernel module of low-
energy-gap organic dyes for efficient conversion of sunlight to electricity. Energy Environ. Sci. 2015, 8, 3192–3197.

(15) Clifford, J. N.; Martínez-Ferrer, E.; Viteris, A.; Palomares, E. Sensitizer molecular structure–device efficiency relationship in doped sensitized solar cells. Chem. Soc. Rev. 2011, 40, 1635–1646.

(16) Lin, R. Y.; Yen, Y. S.; Cheng, Y. T.; Lee, C. P.; Hsu, Y. C.; Chou, H. H.; Hsu, C. Y.; Chen, Y. C.; Lin, J. T.; Ho, K. C.; Tsai, C. Dihydrophenanthrene-based metal-free dyes for highly efficient co-sensitized solar cells. Org. Lett. 2012, 14, 3612–3615.

(17) Rudolph, M.; Yoshida, T.; Miura, H.; Schlettwein, D. Improvement of Light Harvesting by Addition of a Long-Wavelength Absorber in Dye-Sensitized Solar Cells Based on ZnO and Indoline Dyes. J. Phys. Chem. C 2015, 119, 1298–1311.

(18) Sobis, J.; Karolczak, J.; Komar, D.; Anta, J. A.; Zió³ek, M. Transient states and the role of excited state self-quenching of indole dyes in complete dye-sensitized solar cells. Dyes Pigm. 2015, 113, 692–701.

(19) Roy, J. K.; Kar, S.; Leszczynski, J. Revealing the Photophysical Mechanism of N,N’-Diphenyl-aniline Based Sensitizers with the D-D−π-A Framework: Theoretical Insights. ACS Sustainable Chem. Eng. 2020, 8, 13328–13341.

(20) Prabavathy, N.; Shalini, S.; Basalsundaram, R.; Velauthapillai, D.; Prasanna, S.; Walke, P.; Muthukarasiyam, N. Effect of solvents in the extraction and stability of anthocyanin from the petals of Caesalpinia pulcherrima for natural dye sensitized solar cell applications. J. Mater. Sci.: Mater. Electron. 2017, 28, 9882–9892.

(21) Megala, M.; Mayandi, J.; Rajkumar, B. J. M. Optical absorption study of anthoxanthin based natural dyes for dye sensitized solar cells: Experimental and theoretical investigations. Mater. Lett. 2020, 276, No. 128089.

(22) Han, L.; Wu, H.; Cui, Y.; Zu, X.; Ye, Q.; Gao, J. Synthesis and density functional theory study of novel coumarin-type dyes for dye sensitized solar cells. J. Photochem. Photobiol., A 2014, 290, 54–62.

(23) Hara, K.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. Novel Polyene Dyes for Highly Efficient Dye-Sensitized Solar Cells. Chem. Commun. 2003, 34, 252–253.

(24) Wu, F.; Lee, L. T. L.; Liu, J.; Zhao, S.; Chen, T.; Wang, M.; Zhong, C.; Zhu, L. Novel organic dyes based on diarylmethylene-bridged triphenylamine for dye-sensitized solar cells. Synth. Met. 2015, 205, 70–77.

(25) Wu, F.; Zhao, S.; Lee, L. T. L.; Wang, M.; Chen, T.; Zhu, L. Novel D-π-A organic sensitizers containing diarylmethylene-bridged triphenylamine and different spacers for solar cell application. Tetrahedron Lett. 2015, 56, 1233–1238.

(26) Dall’Agnese, C.; Komatsu, K.; Koshiba, M.; Dai, M.; Ching, M. C.; Morì, S. Enhancement of quantum efficiency by co-adsorbing small juliolidine dye and bulky triphenylamine dye in dye-sensitized solar cells. J. Photochem. Photobiol., A 2018, 403–410.

(27) Tarsang, R.; Promarak, V.; Sudyoadduk, T.; Namuangruk, S.; Jungnuttisong, S. Tuning the electron donating ability in the triphenylamine-based D-π-A architecture for highly efficient dye sensitized solar cells. J. Photochem. Photobiol., A 2014, 273, 8–16.

(28) Li, M.; Koul, L.; Diao, L.; Zhang, Q.; Li, Z.; Wu, Q.; Lu, W.; Pan, D. Theoretical Study of Acene-Bridged Dyes for Dye-Sensitized Solar Cells. J. Phys. Chem. A 2015, 119, 3299.

(29) Qian, X.; Zhu, Y. Z.; Chang, W. Y.; Song, J.; Pan, B.; Lu, L.; Gao, H. H.; Zheng, J. Y. Benzo[a]carbazole-Based Donor-π-Acceptor Type Organic Dyes for Highly Efficient Dye-Sensitized Solar Cells. ACS Appl. Mater. Interfaces 2015, 7, 9015.

(30) Sen, A.; Grofj, A. Effect of Electron-Withdrawing/-Donating Groups on the Sensitizing Action of the Novel Organic Dye “3-(S-(4-(Dihydrophenanthren-2-yl)-2-cyanoacrylic Acid) for N-Type Dye-Sensitized Solar Cells: A Theoretical Study. J. Phys. Chem. C 2020, 124, 8526–8540.

(31) Naik, P.; Elmosry, M. R.; Su, R.; Babu, D. D.; El-Shafei, A.; Adhihari, A. V. New carbazole based metal-free organic dyes with D-π-A-A architecture for DSSCs: Synthesis, theoretical and cell performance studies. Sol. Energy 2017, 153, 600–610.
chromophore featuring a binary pi-conjugated spacer. *Chem. Commun.* 2009, 2198–2200.

(51) Sowmiya, M.; Senthilkumar, K. Opto-electronic and interfacial charge transfer properties of azobenzene dyes on anatase TiO2 (001) surface — The effect of anchoring group. *J. Photochem. Photobiol., A* 2017, 346, 372–381.

(52) Mukaddem, K. T.; Chater, P. A.; Devereux, L. R.; Al Bahri, O. K.; Jain, A.; Cole, J. M. Dye-Anchoring Modes at the Dye–TiO2 Interface of N3- and N749-Sensitized Solar Cells Revealed by Glancing-Angle Pair Distribution Function Analysis. *J. Phys. Chem. C* 2020, 124, 11935–11945.

(53) Yang, Z.; Li, K.; Lin, C.; Devereux, L. R.; Zhang, W.; Shao, C.; Cole, J. M.; Cao, D. Predicting Device Parameters for Dye-Sensitized Solar Cells from Electronic Structure Calculations to Reproduce Experiment. *ACS Appl. Energy Mater.* 2020, 3, 4367–4376.

(54) Bella, F.; Galliano, S.; Falco, M.; Viscardi, G.; Barolo, C.; Grätzel, M.; Gerbaldi, C. Unveiling iodine-based electrolytes chemistry in aqueous dye-sensitized solar cells. *Chem. Sci.* 2016, 7, 4880–4890.

(55) Bożek, P.; Broniowski, W. Size of the emission source and collectivity in ultra-relativistic p-Pb collisions. *Phys. Lett. B* 2013, 720, 250–253.

(56) Sun, Z.; Liang, M.; Chen, J. Kinetics of Iodine-Free Redox Shuttles in Dye-Sensitized Solar Cells: Interfacial Recombination and Dye Regeneration. *Acc. Chem. Res.* 2015, 48, 1541–1550.