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Rational molecular engineering of porphyrins for enhanced performance in dye-sensitized solar cells†

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Porphyrin dyes are promising sensitizers for high-efficiency dye-sensitized solar cells (DSSCs) due to their remarkable light-harvesting capabilities. However, realizing their full potential in photovoltaic devices necessitates meticulous optimization of their molecular structure. This study explores the structure–performance relationship in nine novel porphyrin dyes (TZ1–TZ9), aiming to enhance the overall power conversion efficiency (PCE). The impact of donor ability and its bulkiness is investigated using bis(4-hexylphenyl)amine and a bulky modified Hagfeldt donor (bis(2',4',6'-tris(hexyloxy)-[1,1'-biphenyl]-4-yl)amine). Indacenodithiophene IDT and thiophene groups are also incorporated as π -spacers to improve the light-harvesting efficiency and increase the overall molecular bulkiness. Furthermore, diverse acceptors (benzothiadiazole, benzotriazole, and cyanoacrylic acid) are introduced to fine-tune photophysical and electrochemical properties. Among these porphyrin dyes, TZ1 exhibits a remarkable PCE of 9.90% (short circuit photocurrent (J_{SC}) = 15.675 mA cm⁻², open circuit photovoltage (V_{OC}) = 0.834 V, and fill factor (FF) = 0.758), surpassing the PCE of 9.20% (J_{SC} = 14.737 mA cm⁻², V_{OC} = 0.817 V, and FF = 0.764) achieved by GY50 under similar fabrication conditions.

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1. Introduction

Driven by escalating fossil fuel depletion and intensifying environmental concerns, the quest for sustainable energy solutions has become a paramount global challenge. Among renewable energy technologies, solar energy stands out as a frontrunner.^{1–4} In this context, dye-sensitized solar cells (DSSCs) have attracted significant interest within the scientific community as a promising technology for future renewable energy systems. This heightened interest stems from their advantageous attributes, encompassing a cost-effective, solution-based fabrication process, a demonstrably minimal environmental impact, and the remarkable ability to show excellent efficiency under low-light conditions.^{5–12}

Crucially, the sensitizer within a DSSC plays a significant role in capturing solar energy and facilitating its conversion into an

electric current. Among the sensitizer types employed in DSSCs (Organic dyes, ruthenium complexes, porphyrins, and natural dyes),^{8,13,14} porphyrin dyes hold significant promise due to their unique properties. These include intense light absorption across the visible spectrum, readily available constituent elements, robust thermal stability, and the ability to tailor their electrochemical properties through molecular engineering.^{15,16}

The meticulous design of porphyrin sensitizers plays a vital role in maximizing the power conversion efficiency (PCE) of DSSCs. To achieve this objective, strategic manipulation of the donor, π -conjugated spacer, and acceptor moieties within the porphyrin scaffold, particularly at the *meso* and β -positions, is essential. These modifications enable better energy level alignment, enhancing the efficient transfer of charge within the molecule. Consequently, improving the light-harvesting efficiency (LHE) and optimized charge dynamics are facilitated within the DSSC architecture.^{15–22} Additionally, incorporating sterically hindered substituents strategically suppresses dye aggregation and reduces charge recombination, thus contributing significantly to the long-term stability and sustained performance of DSSCs.^{21,23–31}

However, early porphyrin-based exhibited low device performance until the YD series of porphyrins was introduced.^{32–36} The YD-series of porphyrins, featuring D- π -A molecular design, boosted both the electron injection efficiency and the light-harvesting, enabling YD2 to achieve a PCE of 11%.³⁷ This advancement paved the way for the synthesis of

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under vacuum to afford a crude product of desilylated porphyrin, which was used without further purification. Afterward, a solution of the desilylated porphyrin, **5** (110.0 mg, 0.256 mmol), Pd₂(dba)₃ (29 mg, 0.032 mmol), AsPh₃ (78 mg, 0.256 mmol), and NEt₃ (1.85 mL, 13.3 mmol) in THF (16 mL) was heated at 85 °C for 12 h. After cooling to room temperature, the catalyst was removed with Celite, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using CH₂Cl₂ as an eluent to give **TZ1** (60 mg, 54%) as a bright green solid. ¹H NMR (400 MHz, CDCl₃): δ 9.98 (d, *J* = 4.6 Hz, 2H), 9.18 (d, *J* = 4.6 Hz, 2H), 8.93 (d, *J* = 4.6 Hz, 2H), 8.70 (d, *J* = 4.6 Hz, 2H), 8.33 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 7.4 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 8.4 Hz, 2H), 0.23 (d, *J* = 8.6 Hz, 4H), 6.99 (d, *J* = 8.5 Hz, 4H), 6.94 (d, *J* = 8.6 Hz, 4H), 5.01 (t, *J* = 7.2 Hz, 2H), 3.95–3.66 (m, 8H), 2.52–2.43 (m, 4H), 2.39 (dt, *J* = 14.9 Hz, 7.4 Hz, 2H), 1.67–1.45 (m, 8H), 1.44–1.09 (m, 22H), 1.09–0.95 (m, 8H), 0.95–0.76 (m, 18H), 0.75–0.57 (m, 25H), 0.57–0.41 (m, 16H). ¹³C NMR (101 MHz, CDCl₃): δ 159.9, 152.3, 151.9, 150.5, 150.4, 150.2, 134.6, 132.2, 132.0, 130.8, 130.6, 130.5, 129.8, 128.7, 128.5, 121.9, 120.8, 114.5, 105.2, 68.6, 57.1, 35.2, 31.8, 31.7, 31.5, 31.4, 30.2, 29.1, 28.6, 28.6, 28.4, 26.7, 25.1, 22.6, 22.2, 14.1, 13.7. MALDI-MS (HRMS): *m/z* calcd. for C₁₁₁H₁₄₀N₈O₆Zn: [M]⁺ 1745.0187; found 1745.0182.

2.1.2 Procedure for synthesis of TZ2. To a solution of **4** (72 mg, 0.034 mmol) in THF (5 mL) was added tetra-*n*-butylammonium fluoride solution 1.0 M in THF (0.34 mL, 0.34 mmol). After stirring at room temperature for 10 min, the mixture was extracted with CH₂Cl₂/H₂O. The organic layer was collected and dried over Na₂SO₄, then the solvent was removed under a vacuum to afford a crude product of desilylated porphyrin, which was used without further purification. Afterward, to a solution of the desilylated porphyrin, **8** (34.0 mg, 0.102 mmol), Pd₂(dba)₃ (15.6 mg, 0.017 mmol), AsPh₃ (41.6 mg, 0.136 mmol), and NEt₃ (1 mL, 7.19 mmol) in THF (5 mL) was heated at 85 °C for 12 h. After cooling to room temperature, the catalyst was removed with Celite, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using CH₂Cl₂ as eluent to give **TZ2** (31 mg, 40%) as a yellow-brown solid. ¹H NMR (400 MHz, CDCl₃): δ 10.01 (s, 2H), 9.28 (s, 2H), 8.96 (s, 2H), 8.68 (s, 2H), 8.23 (d, *J* = 21.3 Hz, 5H), 7.96 (d, *J* = 6.8 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 4H), 7.17 (d, *J* = 7.3 Hz, 4H), 6.99 (d, *J* = 7.8 Hz, 4H), 6.15 (s, 4H), 4.06–3.45 (m, 20H), 1.76 (s, 4H), 1.60 (s, 8H), 1.51–1.40 (m, 4H), 1.40–1.12 (m, 34H), 1.12–0.95 (m, 8H), 0.95–0.84 (m, 8H), 0.78 (s, 20H), 0.70–0.19 (m, 42H). ¹³C NMR (101 MHz, CDCl₃): δ 159.9, 159.3, 157.9, 152.3, 152.1, 150.8, 150.5, 150.3, 131.8, 131.7, 130.4, 129.2, 125.9, 121.2, 121.0, 114.6, 113.4, 105.2, 93.1, 68.7, 68.0, 31.6, 31.4, 31.3, 29.3, 29.0, 28.6, 28.5, 25.7, 25.5, 25.1, 22.6, 22.5, 22.2, 14.0, 13.7. MALDI-MS (HRMS): *m/z* calcd. for C₁₃₉H₁₇₉N₇O₁₂SZn: [M]⁺ 2234.2624; found 2234.2618.

2.1.3 Procedure for synthesis of TZ3. To a solution of **4** (100 mg, 0.047 mmol) in THF (5 mL) was added tetra-*n*-butylammonium fluoride solution 1.0 M in THF (0.47 mL, 0.47 mmol). After stirring at room temperature for 10 min, the mixture was extracted with CH₂Cl₂/H₂O. The organic layer was

collected and dried over Na₂SO₄, then the solvent was removed under a vacuum to afford a crude product of desilylated porphyrin, which was used without further purification. Afterward, to a solution of the desilylated porphyrin, **5** (80.46 mg, 0.186 mmol), Pd₂(dba)₃ (21.4 mg, 0.023 mmol), AsPh₃ (57.3 mg, 0.187 mmol), and NEt₃ (2 mL, 15.4 mmol) in THF (10 mL) was heated at 85 °C for 12 h. After cooling to room temperature, the catalyst was removed with Celite, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using CH₂Cl₂ as eluent to give **TZ3** (52 mg, 48%) as a green solid. ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 2H), 9.29 (s, 2H), 8.93 (s, 2H), 8.68 (s, 2H), 8.31 (d, *J* = 14.1 Hz, 4H), 8.08 (s, 1H), 7.85 (s, 1H), 7.68 (s, 2H), 7.34 (s, 4H), 7.18 (s, 4H), 7.00 (s, 4H), 6.16 (s, 4H), 5.01 (s, 2H), 4.09–3.63 (m, 20H), 2.51–2.24 (m, 2H), 1.88–1.69 (m, 4H), 1.69–1.54 (m, 8H), 1.53–1.11 (m, 48H), 1.10–0.96 (m, 8H), 0.95–0.85 (m, 10H), 0.85–0.70 (m, 20H), 0.70–0.26 (m, 44H). ¹³C NMR (101 MHz, CDCl₃): δ 159.9, 159.3, 157.9, 152.2, 150.8, 150.5, 150.2, 132.0, 131.8, 130.6, 129.7, 128.5, 125.9, 121.2, 121.0, 114.4, 113.5, 105.2, 93.1, 68.7, 68.0, 57.1, 31.8, 31.6, 31.4, 31.3, 30.2, 29.3, 29.1, 29.0, 28.6, 28.5, 26.7, 25.7, 25.5, 25.2, 22.6, 22.5, 22.2, 14.1, 14.0, 13.7. MALDI-MS (HRMS): *m/z* calcd. for C₁₄₇H₁₉₆N₈O₁₂Zn: [M]⁺ 2329.4264; found 2329.4259.

2.1.4 Procedure for synthesis of TZ4. To a solution of **4** (150 mg, 0.071 mmol) in THF (5 mL) was added tetra-*n*-butylammonium fluoride solution 1.0 M in THF (0.71 mL, 0.71 mmol). After stirring at room temperature for 10 min, the mixture was extracted with CH₂Cl₂/H₂O. The organic layer was collected and dried over Na₂SO₄, then the solvent was removed under vacuum to afford a crude product of desilylated porphyrin, which was used without further purification. Afterward, to a solution of the desilylated porphyrin, **11** (263 mg, 0.212 mmol), Pd₂(dba)₃ (32 mg, 0.035 mmol), AsPh₃ (86 mg, 0.283 mmol), and NEt₃ (1 mL, 7.19 mmol) in THF (5 mL) was heated at 85 °C for 12 h. After cooling to room temperature, the catalyst was removed with Celite, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using CH₂Cl₂ as eluent to give **TZ4** (100 mg, 45%) as a red solid. ¹H NMR (400 MHz, CDCl₃): δ 9.53 (d, *J* = 4.7 Hz, 2H), 9.21 (d, *J* = 4.5 Hz, 2H), 8.80 (d, *J* = 4.5 Hz, 2H), 8.61 (d, *J* = 4.7 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 8.08–8.04 (m, 3H), 7.92 (s, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 8.4 Hz, 2H), 7.57–7.52 (m, 3H), 7.29–7.26 (m, 11H), 7.13–7.09 (m, 13H), 6.92 (d, *J* = 8.4 Hz, 4H), 6.09 (s, 4H), 3.89–3.73 (m, 24H), 2.56 (dd, *J* = 15.2, 5.6 Hz, 10H), 1.71 (t, *J* = 7.6 Hz, 6H), 1.58–1.40 (m, 103H), 1.34–1.22 (m, 55H), 1.16–1.15 (m, 21H), 0.97–0.93 (m, 9H), 0.86–0.82 (m, 23H), 0.71 (dd, *J* = 10.4, 3.6 Hz, 24H), 0.55–0.37 (m, 55H). ¹³C NMR (101 MHz, CDCl₃): δ 159.9, 157.9, 141.7, 131.7, 130.4, 129.2, 128.5, 128.0, 121.2, 110.0, 105.1, 93.0, 77.2, 77.0, 76.8, 75.6, 68.7, 68.6, 35.6, 31.7, 31.6, 31.4, 29.3, 29.2, 29.0, 28.6, 28.5, 25.7, 25.5, 25.1, 22.6, 22.5, 22.2, 14.1, 14.0, 13.7. MALDI-MS (HRMS): *m/z* calcd. for C₂₀₃H₂₅₁N₇O₁₂S₃Zn: [M]⁺ 3138.7699; found 3137.7694.

2.1.5 Procedure for synthesis of TZ5. To a solution of **4** (150 mg, 0.071 mmol) in THF (5 mL) was added tetra-*n*-butylammonium fluoride solution 1.0 M in THF (0.71 mL, 0.71



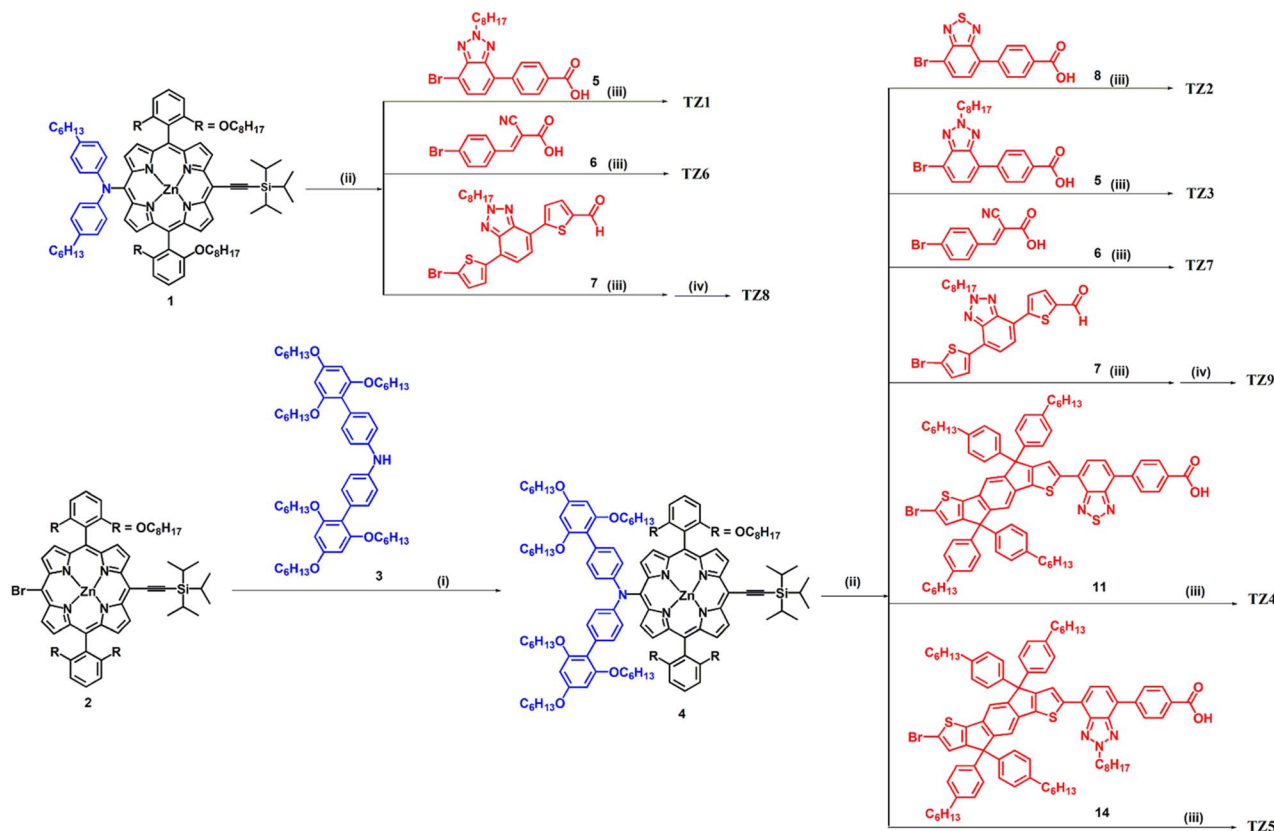
2.1.6 Procedure for synthesis of TZ6. To a solution of **1** (95 mg, 0.061 mmol) in THF (5 mL) was added tetra-*n*-butylammonium fluoride solution 1.0 M in THF (0.61 mL, 0.61 mmol). After stirring at room temperature for 10 min, the mixture was extracted with CH₂Cl₂/H₂O. The organic layer was collected and dried over Na₂SO₄, then the solvent was removed under a vacuum to afford a crude product of desilylated porphyrin, which was used without further purification. Afterward, to a solution of the desilylated porphyrin, **6** (40.0 mg, 0.18 mmol), Pd₂(dba)₃ (20 mg, 0.03 mmol), AsPh₃ (70 mg, 0.24 mmol), and NEt₃ (1.85 mL, 18.0 mmol) in THF (12 mL) were heated at 85 °C for 12 h. After cooling to room temperature, the catalyst was removed with Celite, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Silica gel) using CH₂Cl₂ as eluent to give **TZ6** (48 mg, 48%) as a brown solid. ¹H NMR (400 MHz, CDCl₃): δ 9.64 (d, *J* = 4.6 Hz, 2H), 9.17 (d, *J* = 4.6 Hz, 2H), 8.89 (d, *J* = 4.6 Hz, 2H), 8.68 (d, *J* = 4.6 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.66 (t, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 4H), 6.95 (dd, *J* = 13.0, 8.6 Hz, 8H), 3.84 (dd, *J* = 6.2, 4.3 Hz, 8H), 2.52–2.39 (m, 4H), 1.62–1.44 (m, 6H), 1.26 (s, 28H), 0.98 (dd, *J* = 13.6, 6.7 Hz, 10H), 0.93–0.74 (m, 20H), 0.74–0.55 (m, 28H), 0.48 (dt, *J* = 7.0, 6.1 Hz, 28H). ¹³C NMR (101 MHz, CDCl₃): δ 159.9, 152.2, 152.0, 150.6, 150.4, 134.8, 132.4, 132.2, 131.9, 131.4, 130.7, 130.2, 129.9, 129.7, 128.8, 123.7, 122.0, 120.7, 114.8, 105.3, 95.1, 77.4, 77.1, 76.8, 68.7, 35.3, 32.3, 32.0, 31.8, 31.6, 31.5, 31.0, 29.8, 29.5, 29.2, 28.7, 28.7, 28.5, 28.3, 25.2, 25.1, 22.8,

2.1.8 Procedure for synthesis of **TZ8.** To a solution of **1** (140 mg, 0.066 mmol) in THF (4.7 mL) was added tetra-*n*-butylammonium fluoride solution 1.0 M in THF (0.66 mL, 0.66 mmol). After stirring at room temperature for 10 min, the mixture was extracted with CH₂Cl₂/H₂O. The organic layer was collected, dried over Na₂SO₄, and the solvent was removed under vacuum to afford a crude product of desilylated porphyrin, which was used without further purification. Afterward, to a solution of the desilylated porphyrin, **7** (75.0 mg, 0.15 mmol), Pd₂(dba)₃ (46 mg, 0.05 mmol), AsPh₃ (123 mg, 0.4 mmol), and NEt₃ (2 mL, 20.0 mmol) in THF (5 mL) was heated at 85 °C for 12 h. After cooling to room temperature, the catalyst was removed with Celite, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using CH₂Cl₂ as eluent to get crude as a brown solid. The crude was dissolved in chloroform (5 mL) and added 2-cyanoacetic acid (0.006 g, 0.06 mmol) and piperidine (0.02 mL, 0.13 mmol) and then reacted at 70 °C for 12 h. After cooling to room temperature, the mixture was added to acetic acid (5 mL) and extracted with CH₂Cl₂/H₂O. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using CH₂Cl₂/EA = 4 : 1 as eluent to give **TZ8** (41 mg, 78%) as a brown solid. ¹H NMR (400 MHz, CDCl₃): δ 9.57 (d, *J* =

3.1 Synthesis and characterization

3.2 Optical properties

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Scheme 1 Synthetic routes of TZ porphyrin dyes. (i) $\text{Pd}(\text{OAc})_2$, NaOtBu , $\text{P}(\text{tBu})_3$, toluene. (ii) tetra-*n*-Butylammonium fluoride (TBAF), THF. (iii) $\text{Pd}_2(\text{dba})_3$, AsPh_3 , Et_3N , THF. (iv) 2-cyanoacetic acid, piperidine, CHCl_3 .

Steady-state fluorescence spectra were recorded in THF (Fig. S35[†]). A slight redshift in the fluorescence maximum of **TZ2** was observed, consistent with the trend evident in the absorption spectra. Furthermore, time-resolved fluorescence measurements were conducted using time-correlated single-photon counting (TCSPC) (Fig. S36[†]), and the average fluorescence lifetimes (τ) are summarized in Table 1. Notably, **TZ4** and **TZ5** exhibited longer lifetimes, suggesting their effectiveness in mitigating dye aggregation in dilute solutions.⁴⁵

3.3 Electrochemical properties

Cyclic voltammetry was employed in a three-electrode configuration to investigate the electrochemical behaviours of **TZ** dyes. The electrochemical cell encompassed dry THF, TBAPF₆ as a supporting electrolyte, and ferrocene/ferrocenium as an internal reference electrode (Fig. S37[†]). Potentials obtained *versus* Fc^+/Fc redox couple were meticulously converted to the NHE scale by adding +0.63 V. E_{HOMO} was estimated using the

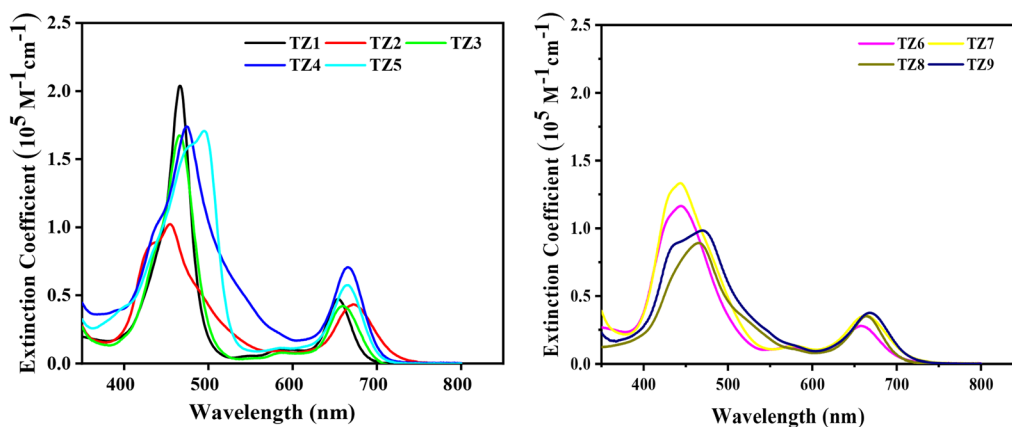


Fig. 2 UV-vis absorption spectra of TZ dyes in THF.

Dye	Absorption ^a $\lambda_{\max}$ (nm) [$\epsilon/10^4$ M ⁻¹ cm ⁻¹]	Emission $\lambda_{\max}$ (nm)	τ_{AV} ^b (ns)	E_{ox} ^c [V]	E_{0-0} ^d [eV]	E_{S1} ^e V	ΔG_{inj} ^f (eV)	ΔG_{reg} ^j (eV)
TZ1	466 (2.0), 654 (0.5)	678	1.56	+0.80	1.86	-1.06	0.56	0.24
TZ2	435 (0.6), 454 (1.0), 772 (0.4)	731	1.54	+0.66	1.77	-1.11	0.61	0.10
TZ3	466 (1.7), 660 (0.4)	691	1.50	+0.67	1.84	-1.17	0.67	0.11
TZ4	474 (1.7), 666 (0.7)	702	2.00	+0.66	1.81	-1.15	0.65	0.10
TZ5	478 (1.6), 495 (1.7), 666 (0.6)	690	2.05	+0.68	1.83	-1.15	0.65	0.12
TZ6	442 (1.16), 659 (0.28)	677	1.26	+0.85	1.86	-1.01	0.51	0.29
TZ7	444 (1.13), 662 (0.34)	694	1.09	+0.75	1.83	-1.08	0.58	0.19
TZ8	465 (0.89), 664 (0.35)	684	1.15	+0.80	1.83	-1.03	0.52	0.24
TZ9	471 (0.98), 666 (0.37)	696	1.00	+0.70	1.81	-1.11	0.61	0.14

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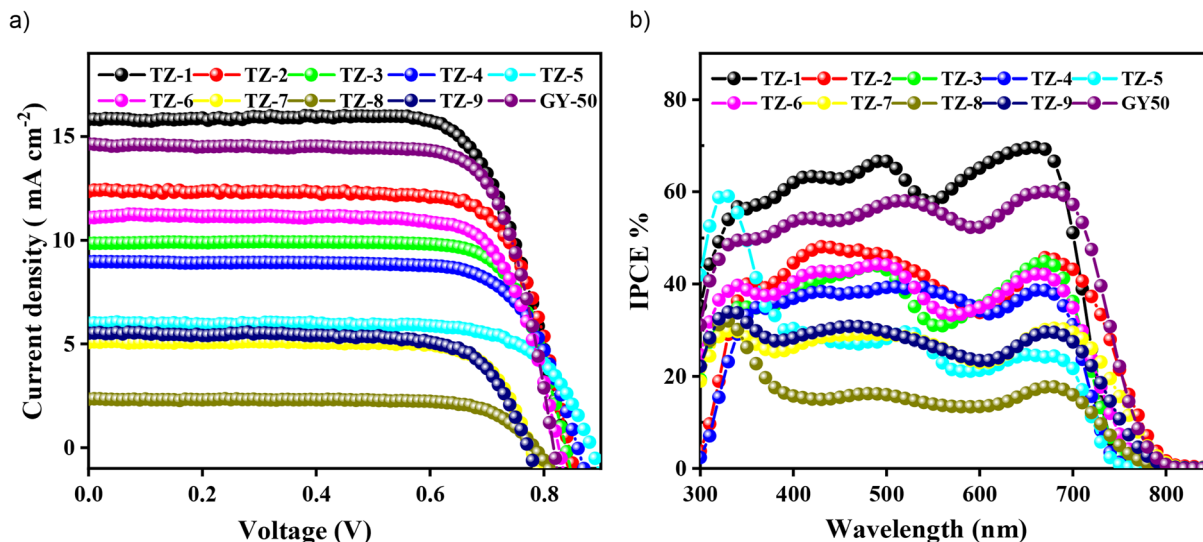


Fig. 4 (a) J - V curves under 1 sun illumination. (b) IPCE spectra of TZ dyes and GY50-based devices.

a larger tilt angle, potentially enhancing charge recombination (low V_{OC}), thereby negating the potential benefits of increased light harvesting achieved by the extended structures.^{6,51–53}

IPCE spectra were employed to further elucidate the light-harvesting capability of the TZ dyes, as presented in Fig. 4b. All investigated dyes displayed characteristic IPCE profiles with two maxima around 480 nm and 700 nm, corresponding to the Soret and Q-band absorption transitions, respectively, with a minor dip observed at approximately 600 nm. The plateau heights in the IPCE spectra follow the trend: **TZ1** > **TZ2** > **TZ6** > **TZ3** > **TZ4** > **TZ5** > **TZ7** ≈ **TZ9** > **TZ8**. This trend is mirrored in the integrated J_{sc} values derived from the IPCE spectra, which closely correlate with the J_{sc} values obtained from the J - V curves, as summarized in Table 2. **TZ1** displays a superior IPCE value of 65%, surpassing its counterparts and the benchmark **GY50** dye (60%). The superiority of **TZ1** could be ascribed to the combination of dye loading capacity, the larger driving force for dye regeneration, and the higher extinction coefficient. On the other hand, **TZ7**, **TZ8**, and **TZ9** showed lower IPCE values due to

the dye aggregation and limitations in charge collection efficiency, as will be investigated using electrochemical impedance spectroscopy.

3.5 Electrochemical impedance spectroscopy study (EIS)

EIS under varying applied potential biases in darkness was employed to investigate the charge collection efficiency (η_{coll}), charge recombination resistance (R_{CT}) at the dye/TiO₂/electrolyte interface, and charge transport resistance (R_T). As shown in Fig. 5a, **TZ2**–**TZ5**-based devices exhibit comparable R_{CT} to **TZ1** despite a lower dye loading, suggesting that strategic bulking of the dye structures suppresses charge recombination through steric hindrance effects. Conversely, **TZ8** and **TZ9** display the lowest R_{CT} despite having the highest dye loading, which can be attributed to dye aggregation.

Consequently, these devices exhibited lower V_{OC} values (0.78–0.79 V, respectively). Notably, the DSSCs-based **TZ1** dye shows the lowest R_T values, as illustrated in Fig. 5b, consistent with its high

Table 2 Photovoltaic parameters of DSSCs-based on TZ and GY50 under AM 1.5G illumination

Dye ^a	J_{sc} [mA cm ⁻²]	V_{OC} [V]	FF	PCE %	J_{sc}^{IPCE} [mA cm ⁻²]	Dye loading ^b [10 ⁻⁸ mol cm ⁻²]
TZ1	15.675 (15.512 ± 0.163)	0.834 (0.826 ± 0.008)	0.758 (0.738 ± 0.014)	9.909 (9.456 ± 0.439)	14.872	6.70
TZ2	12.351 (12.078 ± 0.272)	0.844 (0.846 ± 0.003)	0.759 (0.756 ± 0.003)	7.921 (7.738 ± 0.182)	11.655	4.52
TZ3	9.774 (9.702 ± 0.072)	0.845 (0.845 ± 0.00)	0.785 (0.775 ± 0.010)	6.480 (6.356 ± 0.124)	8.976	3.50
TZ4	9.001 (8.885 ± 0.116)	0.862 (0.859 ± 0.003)	0.746 (0.728 ± 0.018)	5.789 (5.556 ± 0.233)	8.495	3.10
TZ5	5.997 (5.638 ± 0.358)	0.883 (0.872 ± 0.011)	0.736 (0.743 ± 0.007)	3.901 (3.650 ± 0.251)	5.412	2.94
TZ6	11.031 (10.825 ± 0.206)	0.826 (0.824 ± 0.002)	0.770 (0.772 ± 0.002)	7.022 (6.901 ± 0.121)	10.331	8.25
TZ7	5.086 (4.911 ± 0.175)	0.776 (0.777 ± 0.001)	0.773 (0.771 ± 0.002)	3.055 (2.943 ± 0.112)	4.484	7.55
TZ8	2.344 (2.168 ± 0.176)	0.783 (0.786 ± 0.003)	0.753 (0.738 ± 0.015)	1.384 (1.258 ± 0.126)	1.976	10.10
TZ9	5.513 (5.251 ± 0.262)	0.772 (0.770 ± 0.002)	0.732 (0.745 ± 0.014)	3.116 (3.015 ± 0.101)	4.895	8.15
GY50	14.737 (14.779 ± 0.042)	0.817 (0.815 ± 0.002)	0.764 (0.757 ± 0.007)	9.207 (9.133 ± 0.074)	13.812	6.91

^a Photovoltaic parameters were obtained from the champion cells. Averaged values of four independent cells with standard errors are presented in parentheses. ^b The values were obtained by averaging four independent cells.



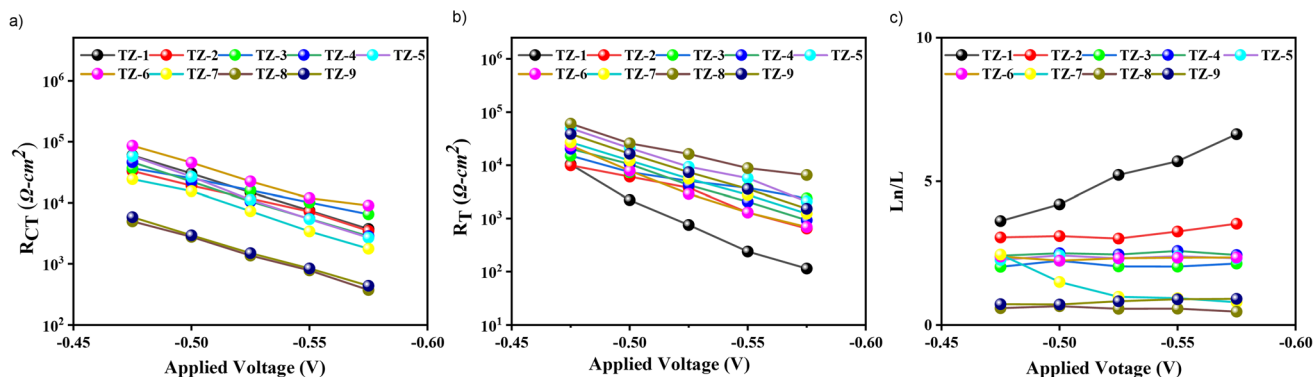


Fig. 5 (a) Logarithmic dependence of charge-recombination resistance. (b) Logarithmic dependence of charge-transport resistance. (c) Charge collection efficiency was calculated by L_n/L ratio.

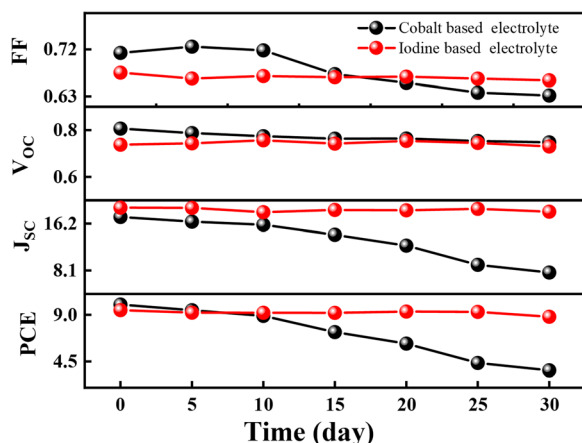


Fig. 6 Stability test TZ1-based DSSCs using cobalt and iodine-based electrolytes at 60 °C.

J_{SC} . Conversely, the elevated R_T observed in the **TZ8**-based DSSC may be attributed to dye aggregation phenomena. This aggregation could impede efficient charge injection, which is consistent with the observed low J_{SC} . Finally, η_{coll} can be quantified using the equation $L_n/L = (R_{CT}/R_T)^{1/2}$, where L denotes TiO_2 thickness, and L_n represents the electron diffusion length. For efficient charge collection, the L_n/L ratio should exceed unity. As shown in Fig. 5c, **TZ7**, **TZ8**, and **TZ9** exhibit lower charge collection efficiencies, providing further evidence for their lower J_{SC} , V_{OC} , and, consequently, lower PCE values. Overall, among the investigated dyes, **TZ1**-based DSSC exhibited the highest PCE of 9.90%, outperforming both the other **TZ** dyes and **GY50** (PCE of 9.20%) under similar fabrication conditions. Conversely, **TZ7**–**TZ9** displayed lower PCEs (3.98%, 1.29%, and 3.52%, respectively) due to insufficient η_{coll} and increased dye aggregation.

3.6 Stability studies of TZ dyes

The photostability of **TZ** dyes was investigated by subjecting dye-coated nanocrystalline TiO_2 films to 1 sun illumination for a day. As illustrated in Fig. S39,† the UV-vis absorption spectra of the dyes showed a slight decrease, demonstrating their photostability.⁵⁴ Moreover, ^1H NMR analysis of powdered dyes

after 24 hours of continuous illumination (Fig. S40 and S41† for **TZ4** and **TZ5** as representative examples) confirmed their structural integrity under prolonged light exposure.

To assess thermal stability, thermogravimetric analysis (TGA) was employed. As presented in Fig. S42,† all **TZ** derivatives exhibited remarkable thermal stability, remaining stable up to 300 °C. To evaluate long-term device performance, DSSCs based on **TZ1** were subjected to aging tests at 60 °C for 30 days, utilizing both cobalt- and iodide-based electrolytes in 3-methoxypropionitrile (MPN). As depicted in Fig. 6, devices employing the iodide-based electrolyte outperformed cobalt-based devices, retaining 92% of their initial PCE compared to only 36%. This disparity could be attributed to the lower volatility of the iodide-based DSSCs.⁶

Furthermore, under continuous indoor illumination at 6000 lux, **TZ1**-based DSSCs maintained 93% and 76% of their initial PCE for iodine and cobalt-based electrolytes, respectively (Fig. S43 and Table S1†). The combination of high thermal and photostability, coupled with acceptable durability, particularly under dim light conditions, positions **TZ** dyes as promising candidates for practical solar energy conversion applications.

4. Conclusion

This study meticulously described the design, synthesis, and performance evaluation of nine novel porphyrin sensitizers, designated as **TZ** dyes, for the application in DSSCs. A systematic investigation was undertaken to explore the structure–performance relationship of these sensitizers. By strategically modifying the donor, π -spacer, and acceptor units, we aimed to understand the critical interplay between molecular design and photovoltaic efficiency. Incorporating a bulky modified Hagfeldt donor resulted in a red-shifted absorption spectrum compared to their counterparts containing alkylamine-based donors. Furthermore, introducing IDT units as π -spacer in **TZ4** and **TZ5** led to enhanced LHE and demonstrably suppressed the charge recombination through steric hindrance effects. These combined effects translated to high V_{OC} values for **TZ4** and **TZ5**. However, this approach comes at the cost of a lower dye loading capacity, consequently leading to a diminished J_{SC} . Further



extension of the π -spacer with thiophene and benzothiadiazole (BTA) moieties in **TZ8** and **TZ9** further red-shifted the absorption spectrum however, it increased the dye aggregation, limiting their photovoltaic performance. All **TZ** dye derivatives exhibited remarkable thermal stability, demonstrating robust structural integrity up to 300 °C. Moreover, these dyes displayed excellent photochemical stability.

Among the investigated dyes, DSSCs based on **TZ1** exhibited a remarkable PCE of 9.90% ($J_{SC} = 15.675 \text{ mA cm}^{-2}$, $V_{OC} = 0.834 \text{ V}$, and $FF = 0.758$), surpassing the PCE of 9.20% ($J_{SC} = 14.737 \text{ mA cm}^{-2}$, $V_{OC} = 0.817 \text{ V}$, and $FF = 0.764$) achieved by the benchmark **GY50** under identical fabrication. Furthermore, the exceptional thermal and photochemical stability of **TZ1**, coupled with its promising long-term operational stability, underscores its potential for practical application in sustainable solar energy conversion technologies.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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