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Novel metal-free organic dyes possessing fused heterocyclic structural motifs for efficient molecular photovoltaics

Ayyanar Karuppasamy,^a Kesavan Stalindurai,^a Jia-De Peng,^b Kuo-Chuan Ho*^b and Chennan Ramalingan*^a

Reported herein are six novel metal free organic dyes such as **PCA1–PCA3** and **PCTA1–PCTA3** featuring fused heterocyclic structural motifs such as phenothiazine and alkylcarbazole. Photophysical/electrochemical properties and nanocrystalline TiO₂ based dye-sensitized solar cell performance of the same have been investigated. Electronic distribution within the molecules has been determined through a computational approach. The overall power conversion efficiencies of the devices with the utilization of dyes **PCA1–PCA3** and **PCTA1–PCTA3** as sensitizers ranges between 4.67 and 8.08%. The novel dyes possessing cyanoacrylic acid as electron acceptor, **PCA1–PCA3**, exhibit higher power conversion efficiency, short-circuit current, open-circuit voltage, and electron lifetime those with thioxothiazolidinylacetic acid, **PCTA1–PCTA3**, as the same. Of the devices fabricated by employing the new metal-free organic sensitizers, that with the dye **PCA2** exerted a power conversion efficiency (PCE, η) of 8.08% with a short circuit current density (J_{SC}) of 16.45 mA cm⁻², an open circuit voltage (V_{OC}) of 735 mV and a fill factor (ff) of 0.68; this PCE is the highest amongst the devices fabricated.

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1 Introduction

Since the existing energy resources (fossil fuels) have been exhausted speedily during recent years, global consciousness is rising in connection with the need to find alternative, renewable energy resources, viz., solar cells, in order to suit the necessities of today's life. In this milieu, sizeable research endeavors have been devoted to dye-sensitized solar cells (DSSCs) since the discovery of ruthenium based cells by Grätzel et al. in 1991¹ with the aim of eco-friendly and inexpensive conversion of solar energy to clean electricity. As a key module of DSSCs, sensitizers play a vital role in light harvesting and electricity conversion, which significantly affect the power conversion efficiency of devices.^{2,3} Although the complexes of polypyridine-ruthenium and porphyrin-zinc are the hitherto best performing sensitizers in DSSCs,^{2,4-15} the former possess the apparent dilemma of heavy metal toxicity as well as resource insufficiency, while the latter have the significant obstacles of poor synthetic yield as well as the handling of highly toxic chemicals. Recently, organic sensitizers have been studied intensively because of their unique features such as economic feasibility, unlimited resources, high

extinction coefficients, and tunable absorption spectra and energy levels.^{16–22} Principally, the performance of organic dyesensitized solar cells is dependent on its electronic and structural uniqueness. It is vital that the energy of LUMO level of the dyes is higher when compared with the energy of the conduction band of the semiconductor for the thermodynamic possibility of charge injection, whereas the dyes which possess broader and strong CT absorption are beneficial for charge generation.²³ Also, it has recently been reported that the recombination of injected electrons with the I^-/I_3^- electrolyte/oxidized dye severely reduces the photocurrent density.²⁴ To encumber the reactions with recombination and contribute to an increase in the shortcircuit current and open-circuit voltage of dye-sensitized solar cell devices, several structural alterations including incorporation of alkyl chains^{25–28} have been made.

To date, a diverse range of novel metal-free organic dyes possessing various structural motifs, including acyclic/cyclic amines and other heterocyclic species have been developed as sensitizers, and notable efficiencies in power conversion have been attained which demonstrate the great potential of metalfree dyes as efficient sensitizers for DSSC applications.^{28–33} Organic sensitizers are generally composed of three structural motifs: an electron donor; a linker with π -conjugation; and an electron acceptor. This structural disposition is favorable for the optimisation of dye-sensitized solar cells performance by modifying/ changing diverse parts in the molecules.³⁴ Organic materials



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^a Department of Chemistry, Kalasalingam University, Krishnankoil – 626 126, Tamilnadu, India. E-mail: ramalinganc@gmail.com

^b Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan. E-mail: kcho@ntu.edu.tw



Fig. 1 Structure of novel metal-free organic dyes PCA1–PCA3 and PCTA1–PCTA3.

containing phenothiazine/carbazole structural components have been used in a range of electronic devices, including DSSCs and OLEDs.^{35–52} We herein report the synthesis, photo-physical, computational, electrochemical, and photovoltaic characteristics of six novel organic dyes possessing alkylcarbazole, phenothiazine and cyanoacrylic acid or thioxothiazolidinylacetic acid structural motifs, as given in Fig. 1.

The design of the aforementioned novel organic dyes is based on the following factors: (i) the butterfly (non-planar) conformation of phenothiazine could satisfactorily hinder aggregation of the molecule and the formation of intermolecular excimers;^{53,54} (ii) the presence of a bulky alkyl carbazole moiety at the 10-position of phenothiazine could also inhibit dye-aggregation, increase the electron life-time of the dyes in the nanocrystalline TiO₂ conduction band, and improve charge separation at the oxide-solution interface;^{28,55} (iii) the presence of electron-rich sulfur and nitrogen heteroatoms could cause the phenothiazine to donate electrons efficiently; (iv) the delocalization of π -electrons could be spread over the complete phenothiazine chromophore, as the two fused aryl scaffolds have been set in an undersized angle (torsion) related to the sulfur and nitrogen atoms; (v) appropriate alkyl functionalities could improve the water tolerance in the electrolytes/improve the solubility and restrict aggregation;²⁸ and (vi) cyanoacrylic acid/thioxothiazolidinylacetic acid could act as acceptor/capable anchoring group.

2 Experimental

2.1 General

The reagents used herein are reagent grade and were utilized as-received. All solvents were distilled/dried by employing standard procedures before their utilization. Column chromatography was performed on silica gel (spherical, 100-200 mesh) slurry packed in glass columns. The eluent systems used for individual separations are furnished in the respective experimental procedures. TLC was performed on pre-silica coated aluminium plates (60, F254) and eluted with the solvents specified. All FT-IR spectra were recorded on a Shimadzu IR Tracer-100 in the range of 4000–400 cm⁻¹ using KBr in pellet form, and the spectral features are reported in terms of wavenumber (cm⁻¹). All NMR spectra were recorded on a NMR spectrometer (BRUKER 400 MHz) at 25 °C with the use of tetramethylsilane (TMS) as an internal standard and CDCl₃ as solvent. Microanalyses were performed using the varioMICRO system. Cyclic voltammetry experiments were done at ambient temperature using a three-electrode (conventional) configuration. The three electrodes used were Ag/AgNO₃ as the reference electrode, glassy carbon as the working electrode, and a platinum wire as the auxiliary electrode. The $E_{(1/2)}$ figures were determined using $1/2(E_p^a + E_p^c)$, in which E_p^a is the anodic peak potential and $E_{\rm p}^{\rm c}$ is the cathodic peak potential. The potentials were indicated with respect to the internal standard, ferrocene. In all the experiments, the supporting electrolyte and the solvent were 0.1 M tetrabutylammonium perchlorate and dichloromethane, respectively. Absorption spectra were acquired on a JASCO V-650 UV-Vis spectrophotometer with the utilization of freshly prepared solutions. Computational calculations were executed using the Gaussian 09 program [DFT, B3LYP; 6-31G(d,p)] package.

2.2 Synthetic procedures

The intermediates, 9-butyl-9*H*-carbazole (**2a**), 9-hexyl-9*H*-carbazole (**2b**), 9-octyl-9*H*-carbazole (**2c**), 9-butyl-3-iodo-9*H*-carbazole (**3a**), 9-hexyl-3-iodo-9*H*-carbazole (**3b**), 3-iodo-9-octyl-9*H*-carbazole (**3c**), 3-bromo-9*H*-carbazole (**4a**), 3-bromo-9-ethyl-9*H*-carbazole (**5a**), and 10*H*-phenothiazine-3-carbaldehyde (7) were synthesized by adopting the literature methods.^{56–59}

2.2.1 Synthesis of carbaldehyde 8a. To a solution of 10*H*-phenothiazine-3-carbaldehyde (0.50 g, 2.4 mmol) and 3-bromo-9-ethyl-9*H*-carbazole (0.70 g, 2.5 mmol) in 1,2-dichlorobenzene (DCB; 20 mL) under nitrogen atmosphere, were added copper powder (0.30 g, 4.7 mmol), powdered potassium carbonate (0.90 g, 6.5 mmol) and 18-crown-6 (0.11 g, 0.4 mmol). The reaction mixture was refluxed for 48 h. and filtered after attaining

atmospheric temperature. It was then subjected to evaporation using a rotary evaporator and the mixture was extracted with dichloromethane after the addition of water. The DCM portion was separated, dried on anhydrous sodium sulphate and concentrated using a rotary evaporator. The solid thus obtained was subjected to column chromatography using 5-25% ethylacetate in hexane as eluent to afford pure carbaldehyde 8a. Yield: 0.51 g (51%), m.p. 140–142 °C. IR (KBr, cm⁻¹): ν 3061.0, 2960.7, 2922.7, 2818.0, 2723.7, 1685.8, 1460.1, 1375.3, 1313.4, 1244.1, 1197.8, 1124.5, 1072.4, 1039.6, 1004.9, 927.8, 894.9, 817.8, 777.3, 744.5, 704.0, 653.9, 628.8, 578.6, 518.4, 462.7; ¹H NMR (400 MHz, CDCl₃): δ 9.66 (s, 1H), 8.07–8.05 (m, 2H), 7.65–7.39 (m, 5H), 7.28–7.20 (m, 2H), 6.97 (d, J = 7.20 Hz, 1H), 6.83-6.75 (m, 2H), 6.22-6.17 (m, 2H), 4.45 (q, J = 7.07 Hz, 2H), 1.53 (t, J = 7.20 Hz, 3H); ¹³C NMR (400 MHz, CDCl₃): δ 189.65, 150.04, 143.36, 140.62, 139.48, 130.92, 130.55, 129.91, 127.59, 127.35, 127.08, 126.68, 126.55, 124.90, 123.47, 122.53, 120.77, 119.94, 119.61, 118.91, 116.78, 115.29, 110.68, 109.00, 37.91, 13.91; anal. calcd for C₂₇H₂₀N₂OS: C, 77.12; H, 4.79; N, 6.66; S, 7.62. Found: C, 77.44; H, 4.82; N, 6.62; S, 7.59.

2.2.2 Synthesis of carbaldehyde 8b. A combination of carbaldehyde 7 (0.50 g, 2.4 mmol), 9-butyl-3-iodo-9H-carbazole (0.87 g, 2.5 mmol), Cu powder (0.30 g, 4.7 mmol), 18-crown-6 (0.11 g, 0.4 mmol) and potassium carbonate (0.90 g, 6.5 mmol) in 1,2-DCB (20 mL) under nitrogen atmosphere afforded carbaldehyde **8b** by adopting the above method. Yield: 0.80 g (74%), m.p. 136–138 °C. IR (KBr, cm⁻¹): ν 3053.3, 2953.0, 2924.1, 2854.7, 2727.4, 1683.9, 1595.1, 1573.9, 1552.7, 1492.9, 1465.9, 1373.3, 1317.4, 1284.6, 1249.9, 1199.7, 1157.3, 1128.4, 1076.3, 1043.5, 1002.9, 933.6, 812.0, 783.1, 744.5, 633.5, 599.9, 509.2, 434.0, 408.9; ¹H NMR (400 MHz, CDCl₃): δ 9.60 (s, 1H), 8.01–7.98 (m, 2H), 7.56 (d, J = 8.40 Hz, 1H), 7.46–7.33 (m, 2H), 7.31 (d, J = 1.60 Hz, 1H), 7.21-7.14 (m, 3H), 6.90 (d, J = 7.20 Hz, 1H), 6.75-6.71 (m, 2H), 6.16-6.10 (m, 2H), 4.31 (t, J = 7.20 Hz, 2H), 1.90-1.85 (m, 2H), 1.45–1.40 (m, 2H), 0.95 (t, J = 7.40 Hz, 3H); ¹³C NMR (400 MHz, CDCl₃): δ 189.73, 150.05, 143.35, 141.10, 139.94, 130.86, 129.95, 127.53, 127.36, 127.08, 126.62, 126.55, 124.76, 123.47, 122.45, 122.37, 120.68, 119.90, 119.55, 118.88, 116.76, 115.28, 110.89, 109.21, 43.24, 31.22, 20.67, 13.92; anal. calcd for C₂₉H₂₄N₂OS: C, 77.65; H, 5.39; N, 6.24; S, 7.15. Found: C, 77.88; H, 5.42; N, 6.21; S, 7.11.

2.2.3 Synthesis of carbaldehyde 8c. A combination of carbaldehyde 7 (0.50 g, 2.4 mmol), 9-hexyl-3-iodo-9*H*-carbazole (0.94 g, 2.5 mmol), Cu powder (0.30 g, 4.7 mmol), 18-crown-6 (0.11 g, 0.4 mmol) and powdered K_2CO_3 (0.90 g, 6.5 mmol) in 1,2-DCB (20 mL) under nitrogen atmosphere provided carbaldehyde 8c by employing the above method. Yield: 0.79 g (69%), m.p. 158–160 °C. IR (KBr, cm⁻¹): ν 3067.2, 2964.6, 2927.9, 2816.4, 2728.7, 1768.7, 1666.5, 1595.1, 1409.9, 1369.5, 1315.5, 1249.8, 1207.4, 1145.7, 1078.2, 1014.6, 923.9, 818.8, 792.7, 744.5, 642.3, 626.9, 603.7, 547.8, 509.2, 455.2; ¹H NMR (400 MHz, CDCl₃): δ 9.67 (s, 1H), 8.09–8.05 (m, 2H), 7.63 (d, *J* = 8.40 Hz, 1H), 7.53–7.41 (m, 3H), 7.39 (d, *J* = 6.80 Hz, 1H), 7.26–7.20 (m, 2H), 6.97 (d, *J* = 7.20 Hz, 1H), 6.82–6.77 (m, 2H), 6.23–6.17 (m, 2H), 4.37 (t, *J* =7.40 Hz, 2H), 1.96–1.93 (m, 2H), 1.48–1.45 (m, 2H), 1.37–1.33 (m, 4H), 0.89 (t, *J* = 7.00 Hz, 3H);

¹³C NMR (400 MHz, CDCl₃): δ 189.82, 150.07, 143.34, 141.07, 139.91, 130.82, 130.80, 130.01, 127.54, 127.37, 127.11, 126.65, 126.57, 124.75, 123.50, 122.45, 122.35, 120.69, 119.87, 119.55, 118.86, 116.78, 115.28, 110.93, 109.24, 43.49, 31.61, 29.06, 27.07, 22.62, 14.07; anal. calcd for $C_{31}H_{28}N_2OS$: C, 78.12; H, 5.92; N, 5.88; S, 6.73. Found: C, 78.33; H, 5.89; N, 5.86; S, 6.70.

2.2.4 Synthesis of carbaldehyde 8d. A combination of carbaldehyde 7 (0.50 g, 2.4 mmol), 3-iodo-9-octyl-9H-carbazole (1.01 g, 2.5 mmol), Cu powder (0.30 g, 4.7 mmol), 18-crown-6 (0.11 g, 0.4 mmol) and powdered K₂CO₃ (0.90 g, 6.5 mmol) in 1,2-DCB (20 mL) under nitrogen atmosphere provided carbaldehyde 8d by employing the above method. Yield: 0.71 g (59%), m.p. 145–147 °C. IR (KBr, cm⁻¹): ν 3059.7, 2961.4, 2922.2, 2848.9, 2725.4, 1772.4, 1681.9, 1595.1, 1572.0, 1409.9, 1367.5, 1313.5, 1249.9, 1203.6, 1078.2, 1045.4, 1018.4, 916.2, 815.9, 740.7, 636.5, 549.7, 507.3, 451.3, 428.2, 406.9; ¹H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 8.09–8.05 (m, 2H), 7.63 (d, J = 8.40 Hz, 1H), 7.53-7.41 (m, 3H), 7.39 (d, J = 6.40 Hz, 1H), 7.26-7.21 (m, 2H), 6.97 (d, J = 7.20 Hz, 1H), 6.82-6.77 (m, 2H), 4.37 (t, J = 7.40 Hz, 2H), 1.96–1.92 (m, 2H), 1.48–1.27 (m, 10H), 0.88 (t, I = 7.20 Hz, 3H); ¹³C NMR (400 MHz, CDCl₃): δ 189.84, 150.08, 143.34, 141.06, 131.91, 130.81, 130.78, 130.03, 127.53, 127.38, 127.11, 126.64, 126.58, 124.74, 123.50, 122.45, 122.34, 120.69, 119.86, 119.55, 118.85, 116.78, 115.28, 110.93, 109.24, 43.49, 31.67, 29.42, 29.25, 29.10, 27.42, 22.67, 14.15; anal. calcd for C₃₃H₃₂N₂OS: C, 78.53; H, 6.39; N, 5.55; S, 6.35. Found: C, 78.79; H, 6.41; N, 5.52; S, 6.33.

2.2.5 Synthesis of dye PCA1. To a solution of carbaldehyde 8a (200 mg, 0.48 mmol) in dry acetonitrile (10 mL), were added piperidine (10 µL, 0.10 mmol) and cyanoacetic acid (60 mg, 0.71 mmol). The mixture was refluxed under nitrogen for 8 h. After attaining ambient temperature, it was evaporated using a rotary evaporator and the mixture was extracted with dichloromethane after dilution with water. The DCM phase was separated, dried using sodium sulphate, and evaporated. The crude thus obtained was then subjected to column chromatography by employing 10-20% methanol in ethyl acetate as eluent to provide the target dye, PCA1. Yield: 183 mg (78%), m.p. 275-278 °C. IR (KBr, cm⁻¹): ν 3057.2, 2966.5, 2877.8, 2821.9, 2223.9, 1678.1, 1564.3, 1489.1, 1465.9, 1327.0, 1302.0, 1257.6, 1209.4, 1089.8, 1020.3, 945.1, 883.4, 802.4, 746.5, 642.3, 594.1, 551.6, 461.0, 424.3; ¹H NMR (400 MHz, CDCl₃): δ 7.98–7.87 (m, 4H), 7.49–7.41 (m, 3H), 7.33-7.25 (m, 3H), 6.90-6.81 (m, 1H), 6.73-6.70 (m, 2H), 6.07 (bs s, 2H), 4.36 (br s, 2H), 1.35 (br s, 3H); anal. calcd for C30H21N3O2S: C, 73.90; H, 4.34; N, 8.62; S, 6.58. Found: C, 74.11; H, 4.36; N, 8.59; S, 6.55.

2.2.6 Synthesis of dye PCA2. A mixture of carbaldehyde **8b** (215 mg, 0.48 mmol), cyanoacetic acid (60 mg, 0.71 mmol), and piperidine (10 µL, 0.10 mmol) in dry acetonitrile (10 mL) gave the target dye PCA2 by adopting the above method. Yield: 185 mg (75%), m.p. 240–242 °C. IR (KBr, cm⁻¹): ν 3050.4, 2956.8, 2870.1, 2218.1, 1676.1, 1560.4, 1487.1, 1464.0, 1319.3, 1300.0, 1280.7, 1255.7, 1205.5, 1166.9, 931.6, 906.5, 873.8, 806.3, 765.7, 740.7, 661.6, 638.4, 594.0, 460.9, 420.5; ¹H NMR (400 MHz, CDCl₃): δ 8.11–7.99 (m, 2H), 7.76–7.74 (m, 2H), 7.69–7.59 (m, 3H), 7.57–7.47 (m, 2H), 7.43–7.38 (m, 2H), 7.01–6.82 (m, 2H),

6.22 (br s, 2H), 4.45 (br s, 2H), 2.01–1.98 (m, 2H), 1.58–1.54 (m, 2H), 1.06 (br s, 3H); anal. calcd for $C_{32}H_{25}N_3O_2S$: C, 74.54; H, 4.89; N, 8.15; S, 6.22. Found: C, 74.77; H, 4.91; N, 8.12; S, 6.19.

2.2.7 Synthesis of dye PCA3. A mixture of carbaldehyde **8d** (242 mg, 0.48 mmol), cyanoacetic acid (60 mg, 0.71 mmol), and piperidine (10 µL, 0.10 mmol) in dry acetonitrile (10 mL) provided the dye **PCA3** by adopting the above method. Yield: 189 mg (69%), m.p. 230–232 °C. IR (KBr, cm⁻¹): ν 3059.1, 2918.3, 2850.8, 2220.1, 1689.6, 1562.3, 1489.1, 1465.9, 1429.3, 1327.0, 1296.2, 1255.7, 1209.4, 1174.6, 933.6, 914.3, 877.6, 846.8, 767.7, 740.7, 633.5, 640.4, 597.9, 551.6, 453.3, 422.4; ¹H NMR (400 MHz, CDCl₃): δ 8.00–7.89 (m, 3H), 7.56 (br s, 2H), 7.46–7.26 (m, 3H), 7.21–7.18 (m, 2H), 6.89 (br s, 1H), 6.77–6.71 (m, 2H), 6.11 (br s, 2H), 4.31 (br s, 2H), 1.88 (br s, 2H), 1.40–131 (m, 4H), 1.19 (br s, 6H), 0.81 (br, 3H); anal. calcd for C₃₆H₃₃N₃O₂S: C, 75.63; H, 5.82; N, 7.35; S, 5.61. Found: C, 75.38; H, 5.84; N, 7.38; S, 5.63.

2.2.8 Synthesis of dye PCTA1. To a solution of carbaldehyde 8b (270 mg, 0.60 mmol) in glacial acetic acid (20 mL), were added 2-(4-oxo-2-thioxothiazolidin-3-yl)acetic acid (140 mg, 0.73 mmol) and ammonium acetate (25 mg, 0.32 mmol). The mixture was refluxed for 8 h and the solvent was removed using a rotary evaporator after attaining ambient temperature. It was then extracted with DCM after diluting with water. The DCM phase was separated, dried on sodium sulphate, and evaporated using a rotary evaporator. Column-chromatography separation of the crude thus obtained using 10-20% methanol in ethyl acetate as eluent furnished the target dye, PCTA1. Yield: 250 mg (67%), m.p. 290–293 °C. IR (KBr, cm⁻¹): ν 3035.7, 2924.1, 2861.2, 1703.1, 1564.3, 1491.0, 1465.9, 1435.0, 1388.8, 1311.6, 1247.9, 1188.2, 1107.1, 1051.2, 950.9, 802.4, 744.5, 709.8, 615.3, 559.4; ¹H NMR (400 MHz, DMSO-d₆): δ 8.28 (s, 1H), 8.20 (d, J = 6.80 Hz, 1H), 7.90 (d, J = 8.00 Hz, 1H), 7.67 (d, J = 7.60 Hz, 1H), 7.60 (s, 1H), 7.51-7.45 (m, 2H), 7.31 (s, 1H), 7.23-7.19 (m, 1H), 7.12 (d, J = 8.00 Hz, 1H), 7.07 (br s, 1H), 6.87 (br s, 2H), 6.19 (d, J = 8.00 Hz, 1H), 6.11 (br s, 1H), 4.51 (s, 2H), 4.47 (br s, 2H), 1.81 (br s, 2H), 1.39–1.31 (m, 2H), 0.92 (t, J = 7.00 Hz, 3H); anal. calcd for C₃₄H₂₇N₃O₃S₃: C, 65.68; H, 4.38; N, 6.76; S, 15.47. Found: C, 65.91; H, 4.40; N, 6.73; S, 15.42.

2.2.9 Synthesis of dye PCTA2. The title compound, PCTA2 was synthesized from the reaction between carbaldehyde 8c (285 mg, 0.60 mmol) and 2-(4-oxo-2-thioxothiazolidin-3-yl)acetic acid (140 mg, 0.73 mmol) in the presence of ammonium acetate (25 mg, 0.32 mmol) in glacial acetic acid (20 mL) by employing the above method. Yield: 281 mg (72%), m.p. 280–282 °C. IR (KBr, cm⁻¹): ν 3042.4, 2943.4, 2856.3, 1763.9, 1716.6, 1560.4, 1465.9, 1396.5, 1311.6, 1224.8, 1190.1, 1112.9, 1051.2, 952.8, 902.7, 798.5, 744.5, 605.7, 561.3, 511.1, 416.6; ¹H NMR (400 MHz, DMSO-d₆): δ 8.32 (s, 1H), 8.23 (d, J = 8.00 Hz, 1H), 7.92 (d, J = 7.60 Hz, 1H), 7.68 (br s, 2H), 7.53-7.47 (m, 2H), 7.36 (s, 1H), 7.25-7.22 (m, 1H), 7.15 (d, J = 7.60 Hz, 1H), 7.09 (br s, 1H), 6.88 (br s, 2H), 6.21 (d, J = 8.80 Hz, 1H), 6.12 (br s, 1H), 4.70 (s, 2H), 4.48 (br s, 2H), 1.83 (br, s, 2H), 1.38 (br s, 2H), 1.28 (br s, 2H), 0.83 (br s, 3H); anal. calcd for C₃₆H₃₁N₃O₃S₃: C, 66.54; H, 4.81; N, 6.47; S, 14.80. Found: C, 66.37; H, 4.83; N, 6.45; S, 14.85.

2.2.10 Synthesis of dye PCTA3. The title compound, PCTA3 was synthesized from the reaction between carbaldehyde 8d (303 mg, 0.60 mmol) and 2-(4-oxo-2-thioxothiazolidin-3-yl)acetic acid (140 mg, 0.73 mmol) in the presence of ammonium acetate (25 mg, 0.32 mmol) in glacial acetic acid (20 mL) by adopting the above method. Yield: 248 mg (61%), m.p. 250-252 °C. IR (KBr, cm^{-1}): ν 3055.2, 2935.7, 2837.3, 1762.9, 1703.1, 1635.6, 1562.3, 1464.0, 1386.8, 1309.7, 1228.7, 1190.1, 1111.0, 1051.2, 915.4, 898.8, 802.4, 742.6, 609.5, 555.5, 460.9; ¹H NMR (400 MHz, DMSO-d₆): δ 8.29 (s, 1H), 8.20 (d, J = 7.60 Hz, 1H), 7.90 (d, J = 8.00 Hz, 1H), 7.68-7.64 (m, 2H), 7.51-7.45 (m, 2H), 7.33 (s, 1H), 7.22 (d, J = 6.00 Hz, 1H), 7.13–7.07 (m, 2H), 6.87 (br s, 2H), 6.18 (d, J = 8.80 Hz, 1H), 6.11 (br s, 1H), 4.63 (s, 2H), 4.46 (br s, 2H), 1.82 (br s, 2H), 1.34-1.29 (m, 4H), 1.19 (br s, 6H), 0.81 (br s, 3H); anal. calcd for C38H35N3O3S3: C, 67.33; H, 5.20; N, 6.20; S, 14.19. Found: C, 67.54; H, 5.22; N, 6.22; S, 14.14.

2.3 Dye-sensitized solar cell fabrication and characterization

A fluorine doped tin(IV) oxide conducting glass (~80% transmittance; 7 Ω sq⁻¹) was initially cleaned with the help of a cleaner (neutral) and was then washed with water (deionized), and subsequently with acetone as well as 2,3-dimethylbutan-2-ol. To reach good mechanical contact between the film of titanium(IV) oxide and the conducting glass, and also to isolate the surface of the glass (conducting) from the electrolyte, the conducting exterior of the FTO was treated with tetraisopropyl orthotitanate (1000 mg) in ethyleneglycol monomethyl ether (3000 mg) solution. By employing the doctor blade technique, titanium(IV) oxide paste was coated on the aforesaid glass. The dried titanium(IV) oxide film was steadily heated (450 °C) in O₂ atm and accordingly sintered at the same temperature for 0.5 h to coat each titanium(IV) oxide layer.

The titanium(IV) oxide photo-anodes of the dye-sensitized solar cells used in the tests were composed of a 15 µm thick transparent titanium(IV) oxide (13 nm) layer with a scattering titanium(w) oxide (300 nm) layer of 5 µm thickness. The titanium(w) oxide film was immersed in the solution, which contains dye (3 \times 10⁻⁴ M), at ambient temperature for a day after the sintering process at 450 °C followed by cooling (80 °C). The solutions of N719-ruthenium complex (used as a standard/ reference) as well as all the new metal free organic dyes were prepared in a mixture of solvents such as acetonitrile and 2-methylpropan-2-ol (1:1; v/v). The photoanode, dye-sensitized titanium(iv) oxide, thus equipped was kept on a conducting glass (sputtered platinum) electrode, maintaining the electrode couple which was divided by a Surlyn $^{\mathbb{R}}$ film (25 μ m thick). Then, the electrode couple was sealed. The electrolyte was 0.05 M I2, 0.1 M LiI, 0.5 M TBP, 0.6 M DMPII, in an ACN and MPN solvent mixture (1:1 v/v). In the counter electrode, a hole was made previously for the injection of electrolyte. Utilizing a capillary, the injection of electrolyte was done, after which it was sealed. The dye loading measurements were carried out by desorbing the dye from the practical TiO₂ electrode with 0.1 M sodium hydroxide (NaOH) in methanol (CH₃OH) and then measuring the UV/Vis absorption (UV-4802, Unico, USA) to calculate the dye loading by using a pre-constructed calibration curve.

The surface of the DSSCs was sheltered by a cover $(0.16 \text{ cm}^2$ light illuminated area) and subsequently it was illuminated by utilizing a solar simulator. Light-intensity (incident; 0.001 W cm⁻²) was standardized with the help of a standard Si-cell. The width (thickness) of the titanium(IV) oxide film was evaluated using SEM. To record UV-visible spectra, the dyes were layered on the titanium(w) oxide films. The baseline was corrected using a naked titanium(iv) oxide coated FTO substrate. EIS were acquired from the potentiostat/galvanostat, prepared with an FRA2 module (constant light illumination; 0.001 W cm⁻²). The range of frequency examined was 10-65 kHz. The applied bias voltage was set at the open-circuit voltage of the DSSC between the conducting glass-titanium(w) oxide-dye working electrode and the indium tin oxide-platinum counter electrode, initiating from the short circuit conditions; the equivalent AC amplitude was 10 mV. The analysis of the EI spectra was made by an equivalentcircuit model. The IPCE curves were acquired under short-circuit conditions. The source of light was a solar simulator (PEC-L11, class-A quality; AM 1.5G) and the light was focused via a monochromator onto the PV cell. The monochromator was added via the visible-spectrum to produce the IPCE (λ). The I_{SC} (mA cm⁻²) was measured with the help of a potentiostat-galvanostat, and the IRF (incident-radiative-flux; W m⁻²) was recorded with an OD (optical-detector) along with a power-meter.

3 Results and discussion

3.1 Synthesis of novel organic dyes

The synthetic approach for the construction of novel metal free organic dyes PCA1-PCA3 and PCTA1-PCTA3 is furnished in Scheme 1. 9-Alkyl-3-iodo-9H-carbazoles (3a-3c) were synthesized from commercially available 9H-carbazole (1) by adopting a two-step synthetic protocol; alkylation with alkyl halide in the presence of potassium hydroxide at 80 °C followed by iodination using potassium iodide and potassium iodate in acetic acid at 80 °C. 3-Bromo-9-ethyl-9H-carbazole (5a) was synthesized from 9H-carbazole (1) employing a two-step synthetic protocol viz., bromination using N-bromosuccinimide in N,N-dimethyl formamide at 0 °C to ambient temperature followed by ethylation with ethyl bromide in the presence of potassium hydroxide at 80 °C. On the other hand, 3-formyl-10H-phenothiazine (7) was synthesized from commercially available 10H-phenothiazine (6) by formylation using 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane in acetic acid under reflux conditions. The 3a-3c and 5a thus synthesized, upon Ullmann type coupling with 10H-phenothiazine-3-carbaldehyde (7) in the presence of copper powder and potassium carbonate under phase transfer catalytic conditions in 1,2-dichlorobenzene at reflux temperature, formed the corresponding carbaldehydes 8a-8d. The novel dyes PCA1-PCA3 and PCTA1-PCTA3



Scheme 1 Synthesis of novel organic dyes PCA1-PCA3 and PCTA1-PCTA3

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were then synthesized by adopting the Knoevenagel type reaction of corresponding heterocyclic aldehydes with cyanoacetic acid in the presence of piperidine in acetonitrile and 2-(4-oxo-2thioxothiazolidin-3-yl)acetic acid in the presence of ammonium acetate in acetic acid, respectively, under reflux conditions.

3.2 Photophysical properties

The UV-visible spectra of novel organic dyes such as **PCA1–PCA3** and **PCTA1–PCTA3** in dichloromethane and anchored on TiO₂ films are given in Fig. 2. The pertinent data for the same are summarized in Table 1. Apart from the absorption bands appearing below 400 nm, which are ascribed to the localized π - π * electron transitions of the conjugated skeleton, absorption bands occur between 400 and 600 nm corresponding to strong intramolecular charge transfer between the heteroaromatic and cyanoacrylic acid/thioxothiazolidinylacetic acid scaffolds. Of the dyes, those with cyanoacrylic acid as the electron acceptor/anchoring group absorbed at lower wavelengths ($\lambda_{max} = \sim 20$ to 30 nm) compared to those with thioxothiazolidinylacetic acid as the electron acceptor/anchoring group. The rationale for this is



Fig. 2 Absorption spectra of the dyes PCA1–PCA3 and PCTA1–PCTA3 (a) in dichloromethane and (b) on a nanocrystalline TiO₂ semiconductor.

probably the electron-accepting nature of the oxothioxothiazolidine scaffold, which is higher compared to the cyanoacrylic acid moiety. Furthermore, among the dyes possessing a cyanoacrylic acid acceptor such as PCA1, PCA2, and PCA3, the one with a two carbon alkyl chain PCA1 exhibits slightly lower λ_{max} compared to the others, which possess comparatively longer alkyl chains (four carbons and eight carbons). The probable reason is that the increase in length of the alkyl chain imparts a reasonably strong electron donating capability, or it may affect J-aggregation. In the cases of dyes PCTA1-PCTA3 wherein thioxothiazolidinylacetic acid acts as the acceptor moiety, there was no appreciable change in the absorption maxima noticed. This implies that increasing the length of the carbon chains (*i.e.*, beyond four carbons) probably inhibits the dye aggregation and enhances the electron delocalization. Among the dyes with a cyanoacrylic acid acceptor, PCA2 provides the highest molar extinction coefficient. Similarly, among those with a thioxothiazolidinylacetic acid acceptor, PCTA2 exhibits the maximum molar extinction coefficient. The enhanced extinction coefficient values favor light harvesting and consequently photocurrent generation in DSSCs. As can be seen from Table 1, the absorption peaks for PCA1-PCA3 and PCTA1-PCTA3 on transparent TiO₂ films are all blue shifted to some extent compared to the absorption peaks in dichloromethane, which could be ascribed to either H-aggregation and/or deprotonation of the dyes on TiO2.47,60,61

3.3 Electrochemical properties

In order to construct an efficient dye sensitized solar cell, it is vital that there are positive energy off-sets of the molecules of dyes in connection with the nanocrystalline TiO₂ and reduction-oxidation electrolytes, in addition to the light harvesting yield of a dye-adsorbed TiO₂. Hence, the electrochemical behavior of the novel organic dyes **PCA1–PCA3** and **PCTA1–PCTA3** was measured using cyclic voltammetry in dichloromethane solution. The cyclic voltammograms and the related data are furnished in Fig. 3 and Table 1, respectively.

The HOMO energy level and LUMO energy level of the dyes were realized by comparing the dyes' reduction-oxidation potentials with ferrocene's oxidation potential, recorded in similar conditions. Having the aforementioned values in hand, the regeneration viability of the oxidized dyes by electrolyte as well as the thermodynamic feasibility for electron-injection into the conduction band of nanocrystalline TiO₂ were evaluated. As can be seen from Fig. 4, the oxidation potentials of the dyes at the ground state are in the range of 1.10-1.21 V vs. NHE. The oxidation potential of the dyes PCTA1-PCTA3, which contain a thioxothiazolidinylacetic acid acceptor/anchoring moiety, is comparatively higher than that of those having a cyanoacrylic acid acceptor/anchoring group (PCA1-PCA3). Most importantly, the dyes PCA1-PCA3 and PCTA1-PCTA3 hold an oxidation potential sufficiently positive compared to redox the potential of the I^{-}/I_{3}^{-} electrolyte, reported as 0.4 V (vs. NHE), commonly employed in DSSCs. Hence, the oxidized species could be regenerated efficiently by the I⁻/I₃⁻ electrolyte. Also, the oxidation potential (first) of PCA1-PCA3 and PCTA1-PCTA3 is sufficiently negative when compared to the conduction band edge

Table 1 Optical and electrochemical data of the dyes PCA1-PCA3 and PCTA1-PCTA3

Dye	$\lambda_{ m max}$, nm ($\epsilon/ m M^{-1}~ m cm^{-1}~10^3$)	FWHM (nm)	λ_{\max} on TiO ₂ (nm)	$\begin{array}{c} E_{\rm ox}{}^{a} ({\rm V}) \\ (\Delta E_{\rm p}, {\rm mV}) \end{array}$	HOMO ^b (eV)	LUMO ^c (eV)	$\frac{E_{0-0}}{(eV)}^d$	$E_{0-0}^{*^{e}}$ (V)
PCA1	471 (10.1)	112	440	0.418(0.18)	5.218	3.069	2.149	-0.961
PCA2	478 (18.9)	109	442	0.437 (0.23)	5.237	3.043	2.194	-0.987
PCA3	480 (16.1)	104	441	0.444(0.20)	5.244	3.146	2.098	-0.884
PCTA1	501 (11.4)	113	460	0.327 (0.13)	5.127	3.084	2.043	-0.946
PCTA2	500 (19.8)	109	462	0.363 (0.15)	5.163	3.176	1.987	-0.854
PCTA3	500 (18.5)	111	461	0.348 (0.14)	5.148	3.163	1.985	-0.867

Absorption spectra were measured in dichloromethane (DCM) solution. ^{*a*} Redox potentials are reported with reference to the ferrocene internal standard. ^{*b*} Deduced from the oxidation potential using the formula HOMO = $4.8 + E_{ox}$. ^{*c*} Obtained from the optical band gap and the electrochemically deduced HOMO value. ^{*d*} Calculated from the optical edge. ^{*e*} Excited state oxidation potential *versus* NHE.



Fig. 3 Cyclic voltamograms of the dyes PCA1-PCA3 and PCTA1-PCTA3.



Fig. 4 Energy level diagram displaying the ground and excited state oxidation potentials observed for the dyes **PCA1–PCA3** and **PCTA1–PCTA3**.

of nanocrystalline TiO₂, reported as -0.5 V (ν s. NHE), as it is positioned in the range -0.85 to -0.99 V.⁶² Since the potential difference between the TiO₂ conduction band edge and the

dyes is more than 0.35 V, it is sufficiently enough to furnish the needed thermodynamic feasibility for electron injection to the nanocrystalline TiO_2 conduction band from the dye.³⁴ The results of the potentials of the excited and ground states of the dyes imply that the dyes are anticipated to be suitable as capable sensitizers in TiO_2 -based DSSCs.

3.4 Theoretical approaches

To obtain further insight into the structures of the molecules and the electronic sharing of the FMOs of PCA1-PCA3 and PCTA1-PCTA3, density functional theory (DFT) calculations were prosecuted.⁶³ The frontier molecular orbitals of the dyes at the B3LYP/6-31G(d,p) level are furnished in Fig. 5. In all the dyes, the electron density is largely distributed on the phenothiazine component/carbazole-phenothiazine components in the HOMO state, whereas the electrons are localized mainly on cyanoacrylic acid/thioxothiazolidinylacetic acid unit at the LUMO level. Hence, excitation of electrons from HOMO to LUMO by light induces a facile shift of the electrons from the phenothiazine/carbazole structural motif to the cyanoacrylic acid/thioxothiazolidinylacetic acid moiety. This distribution of electrons causes us to speculate that the electrons which are excited could be adequately injected to the nanocrystalline TiO₂ conduction band through the acceptor moieties. As it is known, a facile charge transfer could occur by recombination of charge between the photo-injected electrons at the interface of semiconductor/dye/electrolyte and the oxidized dye molecules.⁶⁴ Fig. 5 shows that the shape of the phenothiazine is non-planar and thus restrains the aggregation as it exposes the non-aromatic character of phenothiazine, which can reduce the π - π interaction between the dye molecules.⁵⁴ The alkyl carbazole units linked to the nitrogen of phenothiazine increases the bulky nature of the molecules; as a result the formation of eximers and aggregates is averted.

3.5 Photovoltaic performance

The DSSCs were fabricated by the utilization of all the new dyes as sensitizers on nanocrystalline TiO₂ films in conjunction with the liquid electrolytic system. The significant parameters of the dye-sensitized solar cells, such as PCE (η), fill-factor (ff), shortcircuit current density (J_{SC}) and open-circuit voltage (V_{OC}), are provided in Table 2. The *J*–*V* characteristics of the DSSCs, which were recorded under standard global AM 1.5G solar irradiation,



Table 2 Photovoltaic performance parameters of the DSSCs fabricated using the dyes PCA1-PCA3 and PCTA1-PCTA3

S. no.	η (%)	$V_{\rm OC}$ (mV)	$J_{ m SC}~({ m mA~cm}^{-2})$	ff	f_{\max} (Hz)	Electron lifetime, τ_{e} (ms)	R _{Ct2} (ohm)	Adsorbed dye $(\times 10^{-7} \text{ mol cm}^{-2})$
PCA1	7.47 ± 0.2	735 ± 0.5	15.06 ± 0.2	0.68 ± 0.002	7.01	22.69	15.76	1.45 ± 0.03
PCA2	8.08 ± 0.3	735 ± 0.6	16.45 ± 0.3	0.68 ± 0.003	7.01	22.69	15.23	1.43 ± 0.02
PCA3	7.09 ± 0.2	723 ± 0.5	14.43 ± 0.2	0.68 ± 0.002	10.42	15.27	16.21	1.38 ± 0.03
PCTA1	4.67 ± 0.2	656 ± 0.4	10.01 ± 0.2	0.71 ± 0.003	15.52	10.25	19.42	1.28 ± 0.03
PCTA2	5.26 ± 0.2	642 ± 0.5	11.45 ± 0.2	0.72 ± 0.002	18.92	8.41	18.12	1.26 ± 0.02
PCTA3	4.91 ± 0.2	642 ± 0.4	11.26 ± 0.2	0.68 ± 0.003	18.92	8.41	18.71	1.20 ± 0.02
N719	9.02 ± 0.1	745 ± 0.4	17.01 ± 0.2	0.71 ± 0.002	5.75	27.68	13.98	1.36 ± 0.03

are presented in Fig. 6b. Interestingly, the efficiencies for the DSSCs with cyanoacrylic acid-based dyes and thioxothiazolidinylacetic acid-based dyes range from 7.09 \pm 0.2 to 8.08 \pm 0.3% and 4.67 \pm 0.2 to 5.26 \pm 0.2%, respectively, without obvious differences with the change of their alkyl chains. In particular, the DSSC with PCA2 shows the highest efficiency of 8.08 \pm 0.3%, among all the synthesized dyes. Furthermore, the efficiency of the cell with the PCTA2-based dye is the best among the thioxothiazolidinylacetic acid-based dyes (5.26 \pm 0.2%). Table 2 also shows that the cells with cyanoacrylic acid-based dyes possess higher J_{SC} and V_{OC} than cells with thioxothiazolidinylacetic acid-based dyes, and as a result of this the cells with cyanoacrylic acid-based dyes may achieve higher efficiency than the latter, despite the fact that all of the cells show similar ff.54,65-70 Fig. 6a shows dark current measurements for the pertinent DSSCs. This measurement relates to the characteristic of DSSC which prevents electrons from being captured by the electrolyte. The $V_{\rm OC}$ value would be high if electrons find difficulty in recombination. The result shows that the cyanoacrylic acid-based dyes have a lower dark current than the cells with thioxothiazolidinylacetic acid-based dyes, and as a result of this the cells with cyanoacrylic acid-based dyes lead to lower charge recombination and thus higher $V_{\rm OC}$ values. In general, this could be easily understood because, in contrast to larger molecules which create efficient barriers that block the approach of I_3^- towards the surface of nanocrystalline TiO₂, smaller molecules are prone to form firmly packed monolayers as a result of the smaller amount of steric hindrance. However, they show no obvious differences with the change of their alkyl chains.

IPCE values evaluated alongside the wavelength of irradiation for the dye sensitized solar cells are furnished in Fig. 7. All the dyes showed photon-to-electron conversion efficiency in the region of 400–700 nm (wavelength). Specifically, the dyes **PCA1–PCA3** exhibited a very high IPCE in the region of 400–600 nm, while the dyes **PCTA1–PCTA3** displayed moderate values in the region of 400–650 nm. Of all, the dye **PCA2** showed the highest IPCE (75 to >95%). In addition, the power conversion efficiencies of all the dyes range from 4.67–8.08%.



Fig. 6 J-V Characteristics of the DSSCs fabricated using the novel dyes **PCA1–PCA3** and **PCTA1–PCTA3** under (a) dark (b) at 100 mW cm⁻² (AM 1.5G).

Among them, the dyes **PCA1–PCA3** provided much higher efficiencies than the dyes **PCTA1–PCTA3**. The device with using the dye **PCA2** as a sensitizer displayed a short-circuit current density ($J_{\rm SC}$) of 16.45 ± 0.3 mA cm⁻², an open-circuit voltage ($V_{\rm OC}$) of 735 ± 0.6 mV, a fill factor (ff) of 0.68 ± 0.003, and a PCE (η) of 8.08%, which is the highest among the devices fabricated.

3.6 Electrochemical impedance spectroscopy

It is recognized that a high-open circuit voltage could be observed as a result of electrons in fairly large amounts in the nanocrystalline TiO₂ conduction band. The compactness of electrons in the nanocrystalline TiO₂ conduction band may be an outcome of the enhanced efficiency of charge-collection in the analogous DSSC device. To explore the relative charge collection rate in DSSC devices with PCA1-PCA3 and PCTA1-PCTA3 dyes, electrochemical impedance spectra were measured under the illumination of 100 mW cm⁻². In the Nyquist plot (Fig. 8; equivalent circuit 8a) measured at standard illumination conditions for the new metal free dyes, relatively large intermediate semicircles were observed. These signify a large electron transport resistance for their devices in the series and the order is as follows: PCTA1 > PCTA3 > PCTA2 > PCA3 > PCA1 > PCA2. The low electron transport resistance for the dve PCA2 compared to PCA1, PCA2 and PCTA1-PCTA3 suggests the improved electron collection efficiency of the former over the latter. Since the dye possessing comparatively higher power conversion efficiency showed low electron transport resistance, there is a good correlation between the same. Furthermore, the devices guided enhanced photocurrent due to the improved electron collection efficiency.



Fig. 7 IPCE plots of the DSSCs fabricated using the novel dyes **PCA1-PCA3** and **PCTA1-PCTA3**.



Fig. 8 Nyquist plots observed for the DSSCs under illumination conditions; (a) equivalent circuit.

125

100

75

50

25

0

400

IPCE (%)

Consequently, the better performance of the dye PCA2 over the others such as PCA1, PCA2 and PCTA1-PCTA3 may be ascribed to the enhanced electron collection supported by the encouraging electron injection in the former dye. Additionally, as can be seen in Table 2, the CT resistance at the interface of the nanocrystalline TiO₂/dye/electrolyte (R_{Ct2}) is lower in the case of dyes with cyanoacrylic acid acceptor (PCA1-PCA3) relative to the dyes with thioxothiazolidinylacetic acid acceptor (PCTA1-PCTA2), implying effective electron collection for the cyanoacrylic acid dyes. This observation is in accord with the high short-circuit current values observed for the cyanoacrylic acid dyes.

In addition, taking Bode phase plots (Fig. 9) into consideration, the frequency of the peaks obtained in the middle-frequency region can be utilized to judge the lifetime of an electron within the semiconductor (τ_e) , providing an added indication of the charge recombination rate. The electron lifetime data are comparable to the open circuit voltage data. The specific order of electron lifetime as well as open-circuit voltage for the dyes PCA1-PCA3 and PCTA1-PCTA3 is PCA1 pprox PCA2 > PCA3 > PCTA1 > PCTA2 pproxPCTA3. For the determination of the power conversion efficiency of DSSCs, there are two processes that can play a critical role. One is dye aggregation and the other is the injected electrons recombination process on a TiO₂ semiconductor with the electrolyte and/or oxidized dye. However, these processes are also controlled by the difference in energy between the CB of nanocrystalline TiO₂ and the dye's excited state, the bonding between the nanocrystalline TiO_2 and the dye, and the dye regeneration by the redox electrolyte. It is known that the degree of the shift of conduction band generally depends on the nanocrystalline TiO₂ semiconductor/ dye interfacial dipole which, additionally is affected by the electronic coupling between the nanocrystalline TiO₂ semiconductor and the dye. The observed high J_{SC} for the DSSC with PCA2 could be due to the superior electronic interaction between the dye and the nanocrystalline TiO₂ semiconductor. The EIS spectrum of a FTO/TiO2/dye/electrolyte/Pt/ITO device



Fig. 9 Bode phase plots for the DSSCs measured under illumination conditions.

normally exhibits three semicircles in the range between 10 mHz and 65 kHz. The ohmic serial resistance (R_S) corresponds to the overall series resistance. The first semicircle corresponds to the CT resistance at the counter-electrode (R_{Ct1}); at the same time, the second one is for the semiconductor/dye/electrolyte interface (R_{Ct2}). The Warburg diffusion method of I^-/I_3^- in the electrolyte (Z_{w}) is related to the third semicircle. Nevertheless, in this work the conventional diffusion resistance of the redox couple is actually significantly overlapped by R_{Ct2} because of the short length for the diffusion of the I^- ion with the thin spacer utilized (25 µm thick), and due to the utilization of low viscosity solvents in our electrolyte (viscosities of ACN and MPN are 0.37 cp and 1.60 cp, respectively).

4 Conclusions

Six novel metal free organic dyes possessing fused heterocyclic structural units such as phenothiazine and carbazole as an electron donor/spacer and cyanoacrylic acid/thioxothiazolidinylacetic acid as an acceptor/anchoring moiety have been synthesized. The dyes PCA1-PCA3 with a cyanoacrylic acid acceptor motif exhibited comparatively higher power conversion efficiency than the dyes PCTA1-PCTA3 with a thioxothiazolidinylacetic acid acceptor motif. Of the devices fabricated with the new dyes, that with PCA2 showed a PCE of 8.08%, which is the highest among the dyes synthesized, and also an IPCE of 75% to >95%. Well separated electron distribution in the energy levels of the HOMOs and LUMOs of all the dyes was noted. Akin to power conversion efficiency, the dyes PCA1-PCA3 exerted higher values of short-circuit current, open-circuit voltage, and electron lifetime than the dyes PCTA1-PCTA3. The observed high short-circuit current and low CT resistance at the interface of the semiconductor/dye/electrolyte in the device fabricated with the PCA2 supported better electronic interaction between the semiconductor and dye as well as effective electron collection for the device. A research focus in connection with additional structural alterations to attain further enhancement in the power conversion efficiency is in progress.

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