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New organic dyes based on the carbazole– carbazole system as a donor moiety show great abilities as sensitizers in dye-sensitized solar cells, with overall conversion efficiencies reaching >96% of that of the reference N719-based device.



FULL PAPER

D–D–π–A Type Organic Dyes

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Synthesis and Characterization of D–D– π –A-Type Organic Dyes Bearing Carbazole–Carbazole as a Donor Moiety (D–D) for Efficient Dye-Sensitized Solar Cells

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A series of new D–D– π –A-type organic dyes – **CCTnA** (n = 1-3), **CCT3N** and **CCT2PA**, bearing the 3-(3',6'-di-*tert*-butyl-carbazol-N'-yl)-N-dodecylcarbazol-6-yl system as an electron donor moiety (D–D) – were synthesized by convenient methods and successfully utilized as dye sensitizers for dye-sensitized solar cells (DSSCs). The central π -conjugated bridges were made of oligothiophene and oligothiophene-phenylene units, whereas the acceptor groups were either cyanoacrylic acid or cyanoacrylamide. Detailed investigation into the relationship between the structures, spectral and electrochemical properties, and performances of the DSSCs is described. The DSSC devices performed remarkably well, with typical overall conversion efficiencies of 3.60–5.69 %, and op-

Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable, sustained attention because they offer the possibility of low-cost conversion of photoenergy.^[1] To date, DSSCs with validated efficiency records of >11% have been obtained with Ru complex dyes.^[2] More recently, a 17 cm² DSSC submodule consisting of eight parallel cells and displaying a conversion efficiency of >9.9% was fabricated by Sony.^[3] Although there is still room for efficiency improvement in Ru-based DSSCs, Ru dyes are costly, difficult to produce and normally display only moderate ab-

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timal incident photon-to-current conversion efficiencies (IPCEs) exceeding 80%. The devices containing oligothiophene bridging groups performed better than those with oligothiophene-phenylene bridging groups. Of solar cells based on these dyes, the **CCT3A**-based one gave a maximum IPCE value of 84%, a short-circuit photocurrent density (J_{sc}) of 11.31 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.71 V and a fill factor (FF) of 0.71, corresponding to an overall conversion efficiency (η) of 5.69% (>96% of that of the reference N719-based cell, η = 5.92%). This work suggests that the organic dyes based on donor moieties or donor molecular architectures of this type are promising candidates for improvement of the performances of DSSCs.

sorption intensity.^[2,4] Enormous effort is also being dedicated to the development of new and efficient dyes featuring modest cost, ease of synthesis and modification, large molar extinction coefficients, and long-term stability.^[5]

Ru-free organic dyes meet all of these criteria. Although remarkable progress has been made in the use of organic dyes as sensitizers for DSSCs, with efficiencies exceeding 11% having been achieved,^[6] the optimization and simplification of their chemical structures for further improvements in performance is still needed. In terms of electronic structure, the LUMO energy level of a dye has to be higher than the energy of the conductive band (CB) of a TiO₂ electrode for efficient electron injection, whereas the LUMO energy level of the dye has to be lower than the iodide/triiodide (I^{-/} I₃⁻) redox potential for oxidation and regeneration of dye, respectively. Additionally, a high absorption coefficient over a wide range of visible light wavelength is required for lightharvesting efficiency.

In terms of molecular structure, avoidance of unfavourable aggregation of dyes is also necessary to achieve high efficiency. π - π Aggregation can lead not only to selfquenching and reduction of electron injection into TiO₂, but also to instability of the organic dye, due to the formation of excited triplet states and unstable radicals under light irradiation conditions.^[7] Stability of the dye in its ex-

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Figure 1. Molecular structures of the designed dyes.

cited and ionized states is important for efficiency and durability. These requirements occasionally seem to conflict with one another other; great flexibility in molecular design is therefore essentially important. Organic dyes constructed out of donor (D), π -conjugation and acceptor (A) moieties offer such design flexibility, and broad ranges of conversion efficiencies have been achieved by using D– π –A structures.^[6,8] Most of the organic dyes used for highly efficient DSSCs have long π -conjugated spacers between D and A; however, introduction of long π -conjugation segments results in prolonged, rod-like molecules, which can facilitate the recombination of the electrons with I₃⁻ and magnify aggregation between molecules.^[7,9]

Because of such findings, organic dyes with 2D-n-A structures, in which two D moieties are connected to a π spacer, have recently been reported.^[10] These studies suggested that organic dyes with $2D-\pi-A$ structures might achieve better performances than those with the simple D- π -A structures. We have recently reported on a set of new, simple 2D–D– π –A-type organic dyes (CCTT3A) containing а bis(3,6-di-tert-butylcarbazol-9-ylphenyl)aniline donor moiety (2D-D).[11] These dyes showed significant bathochromic shifts (50-79 nm) in their ICT peaks, relative to a simple D– π –A-type organic dye, together with increases in the ε values (1.45–1.48 fold). Their DSSC devices exhibited larger short-circuit photocurrent densities (J_{sc}) and higher overall conversion efficiencies (η) than a solar cell based on a D $-\pi$ -A dye. However, the efficiencies of these DSSCs were somewhat lower than that of the reference N3-based device.

In this work we therefore report on our further structural modification of 2D–D– π –A-type organic dyes in the form of D–D– π –A-type organic dyes (Figure 1). In our design, the 3-(3',6'-di-*tert*-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl system is employed as an electron donor moiety (D–D). Many groups have recently reported that DSSCs based on carbazole-based dyes have shown η values of up to 9.1%, indicating the importance of their further investigation in DSSCs.^[12] In addition, carbazole derivatives have stimulated great interest because of their excellent hole-

transport capabilities and have become classic hole-transporting materials.^[13] Moreover, the bulky, nonplanar structure of this carbazole-carbazole (D-D) moiety might prove valuable for solving the intractable problem of the close π - π aggregation of the dye molecules. Both the 3,6-di-*tert*butyl and the N-dodecyl substituents can not only provide the solubility of the dye, but can also form a hydrophobic blocking layer on the TiO₂ surface to suppress the approach of I^-/I_3^- in the electrolyte to the TiO₂, consequently leading to improvement of the short-circuit photocurrent density $(J_{\rm sc})$.^[14] The use of either cyanoacrylic acid or cyanoacrylamide as electron-accepting and anchoring groups (A) was investigated, as well as the use of either oligothiophene or oligothiophene-phenylene systems as π -spacers (π) linking the two functional moieties. Here we report in detail the synthesis and physical and photophysical properties of these carbazole-carbazole-based dyes. In addition, their properties as dye sensitizers in DSSCs in comparison with dyes N719 and CCTT3A, which contains bis(3,6-di-tertbutylcarbazol-9-ylphenyl)aniline as donor moiety (2D–D), are also reported.

Results and Discussion

Synthesis and Characterization

The dye molecules were synthesized as outlined in Scheme 1. Firstly, the key intermediate 6-bromo-3-(3',6'-ditert-butylcarbazol-N'-yl)-N-dodecylcarbazole (3) was synthesized by Ullmann coupling between 3,6-di-tert-butylcarbazole (1)^[15] and 3,6-dibromo-N-dodecylcarbazole (2),^[16] themselves obtained by alkylation of carbazole with *tert*-butyl chloride and by direct bromination of N-dodecylcarbazole with NBS/THF, respectively. A stoichiometric reaction between 2 (4 equiv.) and 1 (1 equiv.) in the presence of a catalytic system involving CuI as catalyst, (\pm)-*trans*-1,2-diaminocyclohexane as co-catalyst and K₃PO₄ as base in toluene afforded intermediate 3 in a moderate yield of 77%.



Scheme 1. Synthesis of the designed organic dyes.

From 3, the intermediates 6-(5-bromothiophen-2-yl)-3-(3', 6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazole (5) and 6-(5'-bromo-2,2'-bithiophen-5-yl)-3-(3',6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazole (7) were synthesized in an iterative manner by combinations of Suzuki crosscoupling and bromination reactions. Suzuki cross-coupling with thiophene-2-boronic acid catalysed by Pd(PPh₃)₄/ Na₂CO₃ (2 M, aq.) in THF was employed to achieve increased numbers of thiophene units in the molecule, whereas bromination with NBS in THF selectively introduced a bromo function at the α -position of the terminal thiophene ring, allowing further Suzuki cross-coupling to be performed. Suzuki coupling of 3 and 5 with thiophene-2-boronic acid afforded the thiophene compounds 4 and 6 in good yields of 86% and 80%, respectively, whereas bromination of 4 and 6 with NBS gave the brominated intermediates 5 and 7 in 91% and 79% yields, respectively. Subsequent coupling of bromo compounds 3, 5 and 7 with 5-formylthiophene-2-boronic acid under the same Suzuki coupling conditions provided the corresponding aldehydes 8, 9 and 10 in yields of 57%, 63% and 66%, respectively, whereas coupling of the bromo compound 7 with *p*-formylphenylboronic acid yielded the benzaldehyde 11 in a 91% yield.

Final Knoevenagel condensation of these aldehydes with 2-cyanoacetic acid in the presence of a catalytic amount of piperidine in CHCl₃ at reflux for 18 h (Scheme 1) gave the desired cyanoacrylic acid dyes (E)-3-{2-[3-(3',6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]thiophen-5-yl}-2cyanoacrylic acid (CCT1A), (E)-3-{5'-[3-(3',6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]-2,2'-bithiophen-5-yl}-2-cyanoacrylic acid (CCT2A), (E)-3-{5''-[3-(3',6'-di*tert*-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]-2,2':5',2''-terthiophen-5-yl}-2-cyanoacrylic acid (CCT3A) and (E)-3-(4-{5'-[3-(3',6'-di-tert-butylcarbazol-N'-yl)-Ndodecylcarbazol-6-yl]-2,2'-bithiophen-5-yl}phenyl)-2-cyanoacrylic acid (CCT2PA), in yields of 57%, 60%, 67% and 96%, respectively. On the other hand, condensation of the aldehyde 10 with 2-cyanoacetamide, catalysed by NH₄OAc/ AcOH in a THF/CH₃CN mixture at reflux, afforded (E)-3-{5''-[3-(3',6'-di-*tert*-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]-2,2':5',2''-terthiophen-5-yl}-2-cyanoacrylamide (CCT3N) in a 70% yield. The colours of the solid products deepened as the number of thiophene units in the molecules

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increased, from orange for **CCT1A**, to red for **CCT2A**, and finally to dark red for **CCT3A**, **CCT2PA** and **CCT3N**. Their chemical structures were characterized unambiguously by FTIR, ¹H NMR and ¹³C NMR spectroscopy, as well as by HRMS. These compounds show good solubility in most organic solvents, probably as a result of their bulkiness and the *tert*-butyl and dodecyl substituents on the carbazole rings of the donor moiety.

Photophysical and Thermal Properties

UV/Vis absorption spectra of the dyes, measured in CH₂Cl₂, are shown in Figure 2 (a) and the characteristic data are summarized in Table 1. The spectra of the dyes each displayed two characteristic absorption bands. The absorption band at ca. 297 nm corresponded to a localized π - π^* transition in the carbazole donor, whereas the bands at longer wavelengths (ca. 500–550 nm) were attributed to intramolecular charge transfer (ICT) transitions from the carbazole–carbazole donor moiety to the cyanoacrylic acid or cyanoacrylamide acceptors. This was confirmed by a negative solvatochromic shift [i.e., hypsochromic shift of maximum wavelengths (λ_{max}) of the ICT peaks in more polar solvents], whereas the positions of the π - π^* transition peaks were almost independent of solvent polarity (Figure 2, b).

The molar extinction coefficient (ε) values of the ICT bands of the synthesized dyes were moderate to high, ranging from 21010 to 28890 M⁻¹ cm⁻¹. As the number of thiophene units in the molecules increased from one unit in **CCT1A**, two units in **CCT2A** to three units in **CCT3A**, bathochromic shifts and increased molar extinction coefficients (ε) of the ICT peaks were observed. **CCT3A**, with a terthiophene moiety as a π -linkage, exhibited a larger bathochromic shift of the ICT band than **CCT2PA**, containing a bithiophene-phenylene as π -linkage, but **CCT2PA** had a higher ε value.

The optimized geometries of these last two dyes revealed that the π -linkage of **CCT3A** adopted a more planar conformation than that of **CCT2PA**, as illustrated in Figure 3. The dihedral angle between adjacent thiophene rings (T₂– T₃) was near zero in the oligothiophene-type linkage, but the angle between the thiophene (T₂) and phenylene (P) in the bithiophene-phenylene-type linkage was considerably



Figure 2. (a) UV/Vis absorption spectra of dyes in CH_2Cl_2 . (b) UV/Vis absorption spectra of **CCT1A** in different solvents.

larger (17–19°). Use of cyanoacrylamide as an acceptor in **CCT3N** resulted in a red shift in the ICT band relative to that of **CCT3A**. However, **CCT3N** showed a significantly lower ε value. Direct comparison between the optical properties of **CCT3A** and those of **CCTT3A**, with bis(3,6-di*tert*-butylcarbazol-9-ylphenyl)aniline as a donor moiety (2D–D), revealed that **CCT3A** had a narrower absorption spectrum and a lower ε value than **CCTT3A** (abs_{max} = 464 nm, ε = 33926 M⁻¹ cm⁻¹).^[11]

However, the ε values of these synthesized dyes at their ICT bands were considerably larger than that of the standard Ru dye N719 at 535 nm ($\varepsilon = 14400 \text{ M}^{-1} \text{ cm}^{-1}$),^[17] indicating good light-harvesting capabilities. The greater maximum absorption coefficients of the organic dyes allow correspondingly thinner nanocrystalline films, thus avoiding reductions in the mechanical strengths of the films. This

Table 1. Optical, thermal and electrochemical and electronic properties of the dyes.

Dye	Abs _{max} ^[a] [nm]	ϵ [M ⁻¹ cm ⁻¹]	Abs. ^[b] [nm]	$E_{1/2}(\text{ox})^{[c]}$ [V]	$\begin{array}{c} E_{1/2}(\mathrm{red})^{[\mathrm{c}]}\\ [\mathrm{V}] \end{array}$	T _{5d} ^[d] [°C]	$E_{\rm g}^{\rm [e]}$ [eV]	HOMO ^[f] [V]	LUMO ^[f] [V]
CCT1A	433	21952	413	0.99, 1.40	-1.64	357	2.41	-5.36	-2.95
CCT2A	457	23492	433	0.95, 1.11, 1.25	-1.58	379	2.22	-5.27	-3.05
CCT3A	443	27938	442	0.85, 1.19, 1.40	-1.54	342	2.15	-5.21	-3.06
CCT2PA	416	28874	421	0.88, 1.17, 1.41	-1.66	339	2.36	-5.20	-2.84
CCT3N	487	21037	447	0.88, 1.08, 1.17, 1.39	-1.15	335	2.17	-5.28	-3.11
N719	535	14400	—	-	_	_	1.80	-5.05	-3.25

[a] Measured in CH₂Cl₂ solution. [b] Measured as dyes adsorbed on TiO₂ film. [c] Measured by CV with a glassy carbon working electrode, Pt counter electrode and Ag/Ag⁺ reference electrode and 0.1 \times *n*Bu₄NPF₆ as supporting electrolyte in CH₂Cl₂. [d] Measured by TGA at heating rate of 10 °Cmin⁻¹ under N₂. [e] Estimated from the optical onset: $E_g = 1240/\lambda_{onset}$. [f] Calculated from the first oxidation potential: HOMO = $-(E_{onset}^{oo} + 4.44)$; LUMO = HOMO + E_g .

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Figure 3. Schematic views of the ground-state structures for CCT3A (top) and CCT2PA (bottom).

also benefits the electrolyte diffusion in the film and reduces the likelihood of recombination of light-induced charges during transportation.^[18]

The absorption spectra of the synthesized dyes adsorbed on TiO_2 films were slightly blue-shifted relative to their solution spectra (Figure 4, a). Such a phenomenon is commonly observed in the spectral response of other organic dyes, and may be ascribed to H-aggregation of the dye molecules on the TiO_2 surface and/or interaction between the anchoring groups of the dyes and the surface of TiO_2 .^[19] Of these dyes, the absorption spectrum of **CCT3A** is the broadest, which is an advantageous spectral property for light harvesting over the solar spectrum.



Figure 4. (a) UV/Vis absorption spectra of dyes adsorbed on a TiO_2 film. (b) CV curves measured in CH_2Cl_2 containing nBu_4NPF_6 as supporting electrolyte.

The thermal properties of these dyes were investigated by thermogravimetric analysis (TGA). Those results suggested that the synthesized dyes were thermally stable materials with temperatures at 5% weight loss (T_{5d}) well over 335 °C

(Figure 2, d). Such high thermal stability of the dye is important for the lifetimes of solar cells.^[20]

Electrochemical Properties

The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) curves of each dye exhibited multiple quasireversible oxidations and one irreversible reduction (Figure 4). The reduction was attributed to the reduction of the acceptor moiety. The first oxidation wave was consistent with the removal of electrons from the peripheral carbazole unit in the donor moiety to give a radical cation, and the rest corresponded to the oxidation of the remaining donor and oligothiophene moieties. The first oxidation potentials decreased from 0.99 to 0.95 to 0.85 V as the lengths of the π -conjugated bridges increased, as also observed in other oligothiophenes.^[21] Multiple CV scans revealed identical CV curves, with no additional peak at lower potential on the cathodic scan $(E_{\rm nc})$ being observed, suggesting that these dyes were, as expected, electrochemically stable molecules. Electrochemical coupling reactions of this type can be detected in some carbazole derivatives with unsubstituted 3,6-positions^[22] and might occur upon charge separation, which hampers the dye regeneration. It is therefore important that the dyes are electrochemically stable molecules.

The highest occupied molecular orbitals (HOMOs) of the dyes, calculated from the onset oxidation potentials in the CV curves, range from -5.20 eV to -5.36 eV. This is lower than the redox potential of the I^-/I_3^- couple (-5.16 V), so dye regeneration should be thermodynamically favourable and could compete efficiently with recapture of the injected electrons by the dye radical cations. The lowest unoccupied molecular orbitals (LUMOs) of the dyes were estimated from the HOMOs and the energy gaps (E_{g}) obtained from the optical onset. The LUMOs (-2.84 to -3.11 eV) were less negative than the CB-edge energy level of the TiO₂ electrode (-4.00 vs. vacuum), ensuring efficient charge injection from excited dyes to TiO₂. These values were also less negative that the potential of N719 dye (-3.25 eV).^[23] Consequently, all dyes possess sufficient driving force for electron injection from the excited dyes to the conduction band of TiO₂. As a result, all dyes have enough energetic driving force for efficient DSSCs with use of a TiO₂ photocatalyst and the I^-/I_3^- redox couple. Moreover, with their high LUMO potentials these dyes become very attractive for other metal oxide semiconductors with conduction bands more negative than the conduction band of TiO_2 , such as ZnO, Nb₂O₃, SrTiO₃ and their composites,^[24] to achieve high open-circuit voltage (V_{oc}) , resulting in much improved cell efficiency.

Quantum Chemical Calculation

The calculated ground-state molecular structures of the dyes are shown in Figure 3. A major factor behind low conversion efficiencies of many organic dyes in DSSCs is dye

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aggregation at the semiconductor surface.^[25] We therefore designed the bulky donor moiety based on 3,6-di-*tert*-butylcarbarzole connected to the *N*-dodecylcarbazole unit to provide steric hindrance in this part of the molecule. The dihedral angles formed between carbazole (D₁) and carbazole (D₂) planes in all molecules were as large as ca. 58°, resulting in bulky structures that might help to prevent close π - π aggregation between the dye molecules. Noncoplanar geometry can also reduce contact between molecules and enhance their thermal stability.^[26] The aromatic rings of the π -conjugated spacers adopted more planar conformations. This suggested that π electrons from the donor moiety can delocalize effectively to the acceptor moiety, and subsequently transfer to the conduction band of TiO₂.

The ICT behaviour was analysed in terms of the frontier molecular orbital (FMO) contribution. As shown in Figure 5, the results showed the electronic clouds corresponding to the HOMO delocalized over the carbazole-carbazole donor moiety in each dye, whereas the LUMO showed electron distribution delocalized over the π -spacer and acceptor moieties (cyanoacrylic acid anchoring group). The HOMO-LUMO transition thus corresponded to intramolecular charge transfer behaviour. Natural Bond Orbital (NBO) analysis was employed to provide further insight into the effects of ICT in CCT2PA and CCT3A. Table 2 shows the natural charges of the cyanoacrylic acid, phenylene, thiophene and carbazole moieties in the dye molecules. The positive NBO values in the carbazole moiety correspond to the carbazole being an effective double-electron-donor unit. In contrast, the negative NBO charge in the cyanoacrylic acid components revealed that all five dyes trap the electrons in their acceptor units. After computation, it was also found that the natural charge of the cyanoacrylic acid component in the CCT3A dye was -0.20 e, which decreased to -0.14 e on replacement of the thiophene with the phenylene unit in CCT2PA. These results indicated that the insertion of the phenylene ring significantly affected the electron-accepting capability of the acceptor.



Figure 5. The HOMO (bottom) and LUMO (top) orbitals of **CCT3A** and **CCT2PA** calculated with the B3LYP/6–31G(d,p) set (isovalue = 0.02).

In dye-TiO₂ adsorption, the adsorption of a dye through a carboxylic acid group can be either by physisorption (hy-

Table 2. Natural charges (e) of different units in the molecules calculated at the B3LYP/6-31G(d,p) level of theory.

Dye	C-C[a]	T_1	T ₂	T ₃	Р	А
CCT1A	0.08	_	_	0.11	_	-0.20
CCT2A	0.06	_	0.05	0.10	_	-0.20
CCT3A	0.04	0.02	0.04	0.10	—	-0.20
CCT2PA	0.04	0.02	0.04	_	0.06	-0.14

[a] C stands for carbazole, T for thiophene, P for phenylene and A for acceptor.

drogen bonding between an oxygen atom on the TiO₂ surface and a hydrogen atom of the dye) or through chemisorption (the H atom of the carboxylic acid dissociates and a bond is formed between the carboxylic oxygen atoms and the surface titanium atoms of TiO₂; this can be of monodentate ester, bidentate chelating or bidentate bridging type).^[27] Many experimental studies (FTIR) have indicated, however, that carboxylic acids usually adsorb onto a TiO₂ surface through bidentate-type bridging.^[28] Only bidentate bridging adsorption of the synthesized dyes is presented in this study. The adsorption complex was first fully optimized by use of the Perdew–Burke–Ernzerhof (PBE) functional in conjunction with the Double-Numerical with polarization performed in the DMol³ program. Optimized structures of dye-(TiO₂)₃₈ adsorption complexes are shown in Figure 6 (a). The bond lengths between 5c-Ti and O atom of dyes were calculated to be in the 2.08-2.16 Å range. The adsorption energies (E_{ads}) of **CCT***n***A** (n = 1-3) and **CCT2PA** were calculated to be -17.24,-21.19, -23.09and



Figure 6. (a) Optimized bidentate bridging modes of **CCT1A** and **CCT3A** on the $(TiO_2)_{38}$ cluster calculated by PBE/DNP with the DMol³ program. (b) The adsorption data for the dyes onto TiO_2 films measured over a period of 50 h at room temperature (line represents the numerical regression fit).

Dye	Dye uptake ^[b] ($\times 10^{15}$ molecule cm ⁻²)	$J_{\rm sc} \ ({\rm mAcm^{-2}})$	V _{oc} (V)	FF	IPCE _{max} (%)	η (%)	Relative η compared with the reference N719 (η/η_{N719})	Cal. $J_{\rm sc}^{\rm [c]}$ (mA cm ⁻²)
CCT1A	66.80 ± 2.62	7.35	0.74	0.67	82	3.64	68.2%	7.13
CCT2A	76.42 ± 2.23	9.70	0.73	0.68	81	4.80	89.9%	9.64
CCT3A	84.04 ± 2.87	11.31	0.71	0.71	84	5.69	96.1%	11.12
CCT2PA	84.61 ± 2.81	9.94	0.70	0.69	81	4.82	90.3%	9.81
CCTT3A	53.90 ± 0.50	9.98	0.70	0.67	76	4.62	78.0%	9.91
N719	56.11 ± 1.00	11.63	0.71	0.72	81	5.92	100%	11.50

Table 3. Performance parameters of DSSCs constructed with the dyes.^[a]

[a] Experiments were conducted under identical conditions with TiO_2 photoanodes of approximately 11 µm thickness and 0.25 cm² working area on the FTO (8 ohm sq⁻¹) substrates. [b] Obtained from measurement of dye adsorption. [c] Obtained from integration of the corresponding IPCE spectra.

-20.43 kcalmol⁻¹, respectively, indicating strong interactions between the dyes and the TiO₂ surface.

The performance of the DSSC is based not only on the absorption of the harvesting dye but also on the total amount of dye present. Dye uptakes were therefore determined by the reported method.^[29] It was found that the maximum uptake of each dye at equilibrium was 66.80×10^{15} , 76.42×10^{15} , 84.04×10^{15} and 84.61×10^{15} molecules cm⁻² for CCT1A, CCT2A, CCT3A and CCT2PA, respectively (Figure 6, b, and Table 3). Unfortunately, the CCT3N dye was poorly adsorbed on TiO₂, suggesting an ineffective dye sensitizer for DSSC. The lower dye uptake of CCT1A on the TiO₂ film relative to the others can probably be explained in terms of steric hindrance of the donor moiety around the carboxylic acid anchoring group, resulting from the considerably shorter π -spacer of CCT1A as shown in Figure 6 (a). As a result, the dyes CCT3A and **CCT2PA**, with longer π -conjugated spacers, were found to be more spacious for accommodation of the donor moiety, allowing better dye uptake. The chemisorption of all dyes onto the surfaces of TiO₂ films was confirmed by FTIR spectroscopy, which showed absorption peaks both of the dyes and of TiO₂ at 2965 (C−H), 2207 (C≡N), 1611 (C=O), 1508 (C=C), 1365 (C=O), 1317, 1292 and 1226 cm⁻¹. The characteristic carboxylate group vibration modes, symmetric (1365 cm⁻¹) and asymmetric (1611 cm⁻¹), were identical for all the dyes and similar to those reported for other dyes, independent of molecular volume.^[30] This indicates that all such dyes bind to the TiO_2 in the same way, so observed differences in performance can be directly related to the effect of molecular volume and the amount of dye absorbed.

Photovoltaic Properties

These newly synthesized dyes were used as sensitizers for dye-sensitized TiO₂ solar cells (DSSCs). Cells with effective areas of 0.25 cm² (0.5 cm \times 0.5 cm) were fabricated with TiO₂ working electrode, platinum (Pt) counter electrode and an electrolyte composed of 0.03 M I₂/0.6 M LiI/0.1 M guanidinium thiocyanate/0.5 M *tert*-butylpyridine in a 15:85 (v/v) benzonitrile/acetonitrile solution. A reference cell with the same structure but based on N719 dye as the sensitizer was also made for purposes of comparison. For the measurement of the photovoltaic performance, five cells were prepared and measured under the standard conditions. The

corresponding current density/voltage (J/V) characteristics and the incident monochromatic photon-to-current conversion efficiency (IPCE) plots are shown in Figure 7, and the resulting photovoltaic parameters (average values) are summarized in Table 3. The IPCE spectra of CCTnA and **CCT2PA** as sensitizers became broadened and red-shifted as the number of thiophene units in the molecule increased, consistently with the results of the absorption spectra. The maximum IPCE values of all devices were as high as 76-84%, higher than those of the reference N719-based cell, due to the larger molar extinction coefficients of the synthesized dyes, but the N719-based cell showed a broader IPCE spectrum, consistently with its wide absorption spectrum. This suggests that the structure modification of these dyes by use of carbazole-carbazole as donor strongly influences the collection efficiencies, in turn having a significant effect on the IPCEs and overall conversion efficiencies (η) of the devices.



Figure 7. (a) IPCE plots and (b) J/V curves for the DSSCs based on the synthesized dyes and on the reference N719 dye.

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Organic Dyes for Efficient Dye-Sensitized Solar Cells

Under standard AM 1.5G 100 mW cm⁻² illumination conditions, the CCT3A-sensitized cell showed the highest overall efficiency of the three dyes and gave a short-circuit photocurrent density (J_{sc}) of 11.31 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.71 V and a fill factor (FF) of 0.71, corresponding to an overall conversion efficiency (η) of 5.69%. The J_{sc} and η values for the DSSCs were in the order CCT3A (11.31 mA cm⁻², 5.69%) > CCT2PA $(9.94 \text{ mA cm}^{-2}, 4.82\%) > CCT2A (9.70 \text{ mA cm}^{-2}, 4.80\%) >$ CCT1A (7.35 mA cm⁻², 3.64%). The measured J_{sc} values for these solar cells were also cross-checked with the J_{sc} values calculated by integration of their corresponding IPCE spectra (cal. J_{sc}), partly verifying the reported efficiencies and the results found in agreement to within 5% (Table 3). The better solar cell performance (highest η and $J_{\rm sc}$ values) of the CCT3A-based cell in relation to CCT2PA and the other dyes in this series could be explained by the red-shift of the absorption spectrum of CCT3A, which resulted in a better light-harvesting efficiency of CCT3A. The lower efficiency of the CCT1A-based cell relative to CCT2A and CCT3A could be attributed both to the poorer spectral properties and to the lower dye content adsorbed on TiO₂ film. It should be noted that the V_{oc} values of the CCTnAbased DSSCs were as high as 0.74 V. This might be attributable to suppression of dark current owing to the hydrophobic blocking effect of the tert-butyl and the long dodecyl substituents on the carbazole donors shielding the TiO₂ surface from I^{-}/I_{3}^{-} in the electrolyte, thus reducing the charge recombination or dark reaction. The larger size of the carbazole-carbazole group might also effectively hinder self-aggregation of the dyes on a TiO₂ surface. The minimization of interfacial charge recombination losses in the device is also evident from the dark current data for the cells. For the same reason, the performance of the CCT3A-based DSSC in terms of J_{sc} value, FF value and η is superior to that of the CCTT3A-based DSSC (Table 1). The results suggest that the use of the 3-(3',6'-di-tert-butylcarbazol-N'yl)-N-dodecylcarbazol-6-yl moiety (D-D) as a donor has a significant effect on the device performance. The efficiency of the CCT3A-based device reached >96% of that of the reference N719-based cell ($\eta = 5.92\%$). The slightly better efficiency of the N719-based device in relation to its **CCT3A** counterpart originates from its slightly larger J_{sc} value; N719 has a broader IPCE spectrum, which is consistent with its wide absorption spectrum.

Conclusions

In summary, we have synthesized new organic dyes – **CCTnA**, **CCT3N** and **CCT2PA** – containing $3-(3',6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl units as their donor moieties. In their structures, either oligothiophene or oligothiophene-phenylene systems, together with cyano-acrylic acid or cyanoacrylamide units, were used as <math>\pi$ -conjugated linkages and as acceptors, respectively. These dyes displayed high thermal and electrochemical stability, which can enhance the stability of a solar cell. These compounds

exhibited high absorptivity in the blue/green region of solar light. DSSC devices fabricated by use of these materials as dye sensitizers displayed medium to high overall conversion efficiencies (η) ranging from 3.6% to 5.69%. The optimal IPCE value reached beyond 84%.

The structures of the bridges are also influential. The presence of thiophene units in a bridge improves coplanarity, thus promoting better resonance delocalization, whereas the phenylene group is twisted with a large dihedral angle. The performance of the oligothiophene-bridged dye was better than that of the oligothiophene-phenylene type.

The dye containing cyanoacrylamide as an acceptor, however, could not be used as a sensitizer in DSSC, due to its poor adsorption on TiO₂. Out of these dyes, the best performance was found with **CCT3A**, which exhibited a maximum IPCE value of 84%, a $J_{\rm sc}$ value of 11.31 mA cm⁻², a $V_{\rm oc}$ value of 0.71 and a FF value of 0.71, corresponding to an η value of 5.59% (>96% of the reference N719-based cell). This device performs better than that with **CCTT3A** as sensitizer.

The bulkiness of the carbazole–carbazole moiety (D-D) might effectively hinder self-aggregation of the dyes on TiO₂ surfaces, whereas the hydrophobic properties of the *tert*-butyl and the long dodecyl substituents should also minimize the losses due to charge recombination in the device.

Our results suggest that alternative highly efficient organic dyes comparable in performance to Ru complexes could potentially be developed through the use of the 3-(3',6'di-*tert*-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl system as a donor. Development of this dye, based on further broadening of its absorption spectrum to enhance its light harvesting ability through extension of its π -conjugation system, is in progress.

Experimental Section

Materials and Instruments: All reagents were purchased from Aldrich, Acros or Fluka and were used without further purification. All solvents were supplied by Thai companies and used without further distillation. THF was heated at reflux with sodium and benzophenone and distilled prior to use. CH_2Cl_2 for electrochemical measurements was washed with conc. H_2SO_4 and distilled twice from calcium hydride.

¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE 300 MHz spectrometer with TMS as the internal reference in CDCl₃ or CDCl₃/[D₆]DMSO as solvents. Infrared (IR) spectra were measured with a Perkin–Elmer FT-IR spectrum RXI spectrometer as potassium bromide (KBr) discs. UV/Vis spectra were recorded with dilute solutions in spectroscopic grade dichloromethane with a Perkin–Elmer UV Lambda 25 spectrometer. Diffuse reflectance spectra of dye-sensitized TiO₂ samples were measured at room temperature with a Shimadzu UV-3101 spectrophotometer. Barium sulfate was used as a standard. The measured reflectance spectra were then converted into absorption spectra by the Kubelka–Munk method. Thermal gravimetric analyses (TGA) were performed with a Rigaku TG-DTA 8120 thermal analyser and a heating rate of 10 °C min⁻¹ under nitrogen. Cyclic and differential pulse voltammetry (CV and DPV) measurements were carried out

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with an Autolab potentiostat PGSTAT 12 and a three-electrode system (platinum counter electrode, glassy carbon working electrode, and Ag/Ag⁺ reference electrode) at a scan rate of 50 mVs⁻¹ in CH₂Cl₂ with tetrabutylammonium hexafluorophosphate (*n*Bu₄NPF₆) as a supporting electrolyte under argon. The concentrations of analytical materials and electrolyte were 1×10^{-3} M and 0.1 M, respectively. Melting points were measured with an Electrothermal IA 9100 series digital melting point instrument and are uncorrected. HRMS was performed by the Mass Spectrometry Unit, Mahidol University, Thailand.

Dye Adsorption Measurements: The absorption spectra of the initial dye solutions $(2.6-2.7 \times 10^{-5} \text{ M})$ in CH₂Cl₂ were measured with a Shimazu MultiSpec-1501 spectrophotometer. The TiO₂ substrates with active areas of 0.25 cm^2 ($0.5 \text{ cm} \times 0.5 \text{ cm}$), prepared in the same manner as the substrates used for fabrication of DSSCs, were baked at 450 °C for 30 min and allowed to cool to 70–80 °C before immersion into the dye solution in a screw cap quartz cuvette (1 cm × 1 cm). The absorption changes were monitored hourly for 6 h and then every 2 h for 50 h. The amount of dye uptake was calculated from the calibration plot of known dye concentration. The chemisorption of all dyes onto TiO₂ film was characterized with a Perkin–Elmer FT-IR spectrum RXI spectrometer.

Fabrication and Characterisation of DSSCs

Device Fabrication: The photoanodes composed of nanocrystalline TiO₂ were prepared by a previously reported procedure.^[31] Fluorine-doped SnO₂ (FTO) conducting glasses (8 ohm sq⁻¹, TCO30-8, Solaronix) were used for transparent conducting electrodes. The double nanostructure thick film (≈11 µm thickness) consisting of a transparent (Ti-Nanoxide 20T/SP, Solaronix) and a scattering (Ti-Nanoxide R/SP, Solaronix) TiO2 layer were screen-printed on TiCl₄-treated FTO. The thickness of the TiO₂ film was controlled by selection of screen mesh size and repetition of printing. Prior to dye sensitization, the TiO₂ electrode with cell geometry of 0.5×0.5 cm² were treated with an aqueous solution of TiCl₄ $(4 \times 10^{-2} \text{ M})$ at 70 °C in a water saturation atmosphere, heated to 450 °C for 30 min and then allowed to cool to 80 °C. The TiO₂ electrodes were immersed in the dye solution $(3 \times 10^{-4} \text{ M N719 in})$ ethanol, and 5×10^{-4} M organic dyes in CH₂Cl₂) in the dark at room temperature for 30 h to stain the dye onto the TiO₂ surfaces. Excess dye was removed by rinsing with the appropriate solvent. To ensure maximum dye adsorption on the TiO₂ film, dye concentrations higher (>10-fold) than those used for dye adsorption experiments were used. The Pt counter electrode was prepared on a predrilled TCO30-8 FTO glass (Solaronix) by thermal decomposition of H₂PtCl₆ (7 \times 10⁻³ M) in propan-2-ol solution at 385 °C. The dye-adsorbed TiO₂ photoanode and Pt counter electrode were assembled into a sealed cell by heating a gasket Meltonix 1170-25 film (25 µm thickness, Solaronix) as a spacer between the electrodes. An electrolyte solution of I_2 (0.05 M)/LiI (0.1 M)/tetrapropylammonium iodide (0.4 M)/tert-butylpyridine (0.4 M) in a valeronitrile/acetonitrile 15:85 (v/v) mixture was filled through the predrilled hole by a vacuum backfilling method. The hole was capped by use of hot-melt sealing film (Meltonix 1170-25, 25 µm thickness, Solaronix) and a thin glass cover. Finally, Scotch 3M conducting tape and silver paint (SPI supplies) were coated onto the electrodes to enhance the electric contact. For each dye, five devices were fabricated and measured for consistency; averaged cell data are reported. Reference cells with the same device configuration based on N719 dye as the sensitizer were also fabricated for comparison.

Device Characterization: The current density/voltage characteristics of the DSCs were measured with a Keithley 2400 source meter unit in a 4-terminal sense configuration. The data were averaged from

forward and backward scans with bias steps and delay times of 10 mV and 40 ms, respectively, by the method of Koidea and Han.^[32] Simulated sunlight was provided by a Newport sun simulator 96000 with an AM 1.5G filter. To minimize error of measurement, the irradiation intensity of 100 mW cm⁻² was approximated with a calibrated BS-520 Si photodiode (Bunnkoukeiki Co., Ltd., Japan), the spectral response of which was very similar to that of the DSSCs. The spectral output of the lamp was also matched to the standard AM 1.5G solar spectrum in the 350-750 nm region with the aid of a KG-5 filter with spectral mismatch of less than 2% as reported by Yanagida et al.^[33] Incident photon-to-electron conversion efficiencies (IPCEs) of the devices under short-circuit conditions were determined with the aid off an Oriel 150-W Xe lamp fitted with a CornerstoneTM 130 1/8 m monochromator as a monochromatic light source, a Newport 818-UV silicon photodiode as power density calibration and a Keithley 6485 picoammeter. All measurements were performed with use of a black plastic mask with an aperture area of 0.180 cm² and no mismatch correction for the efficiency conversion data.

Quantum Chemical Calculations: Ground-state geometries were fully optimized by use of a DFT level with the B3LYP hybrid functional. All optimizations were calculated without any symmetry constraints with use of the 6-31G(d,p) basis set and the Gaussian 09 software package.^[34] The natural bond orbital analysis (NBO) was obtained with B3LYP/6–31G(d,p). The adsorption of dyes on the (TiO₂)₃₈ cluster was performed by means of DFT calculations and the DMol³ program in Materials Studio version 5.5. The structure of (TiO₂)₃₈ was composed of 38 TiO₂ units that modelled a TiO₂ nanoparticle, as in the researchers' previous report.^[35]

6-Bromo-3-(3',6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazole (3): A mixture of 2 (31.44 g, 63.48 mmol), 1 (4.43 g, 15.87 mmol), CuI (1.51 g, 7.94 mmol), K₃PO₄ (8.42 g, 39.68 mmol) and (±)trans-1,2-diaminocyclohexane (0.90 g, 7.94 mmol) in toluene (200 mL) was stirred at reflux under N₂ for 48 h. Water (50 mL) was added, and the mixture was extracted with CH2Cl2 (50 mL \times 2). The combined organic phase was washed with water (50 mL \times 2) and brine (100 mL), dried with anh. Na₂SO₄ and filtered, and the solvents were removed. Purification by column chromatography over silica gel with elution with a mixture of CH₂Cl₂ and hexane (1:5) followed by recrystallization with a mixture of CH₂Cl₂ and methanol afforded the product (8.43 g, 77%) as a white solid (m.p. 176 °C). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.18-8.15$ (m, 4 H), 7.57-7.45 (m, 3 H), 7.44 (d, J = 1.13 Hz, 2 H), 7.32-7.27 (m, 3 H),4.38 (t, J = 7.20 Hz, 2 H), 1.96 (t, J = 6.90 Hz, 2 H), 1.65–1.25 (m, 36 H), 0.93 (t, J = 6.30 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 139.29, 129.54, 128.42, 123.45, 123.42, 123.24, 111.95, 111.89,$ 111.31, 111.19, 111.10, 110.60, 109.54, 43.36, 31.93, 30.70, 29.95, 29.58, 29.35, 28.84, 28.28, 28.01, 12.74, 27.22, 22.71, 14.82 ppm. FTIR (KBr): $\tilde{v} = 3053$, 2957, 1490, 1362, 1289, 1261, 800 cm⁻¹. HRMS: m/z calcd. for C₄₄H₅₅BrN₂ 690.3549; found 692.3601 [M $+ 2 H]^+$.

6-(Thiophen-2-yl)-3-(3',6'-di-*tert***-butylcarbazol**-*N***'-yl)-***N***-dodecylcarbazole (4):** A mixture of **3** (1.00 g, 1.44 mmol), thiophene-2-boronic acid (0.09 g, 1.21 mmol), Pd(PPh₃)₄ (0.02 g, 0.02 mmol) and Na₂CO₃ solution (2 M, 15 mL) in THF (20 mL) was degassed with N₂ for 3 min. The mixture was heated at reflux under N₂ for 48 h. After the mixture had cooled, water (50 mL) was added, and the mixture was extracted with CH₂Cl₂ (50 mL × 2). The combined organic phase was washed with water (50 mL × 2) and brine (50 mL), dried with anh. Na₂SO₄ and filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel with elution with a mixture of CH₂Cl₂ and hexane



(1:6) gave the product (0.85 g, 86%) as a pearl-white solid (m.p. 132 °C). ¹H NMR (300 MHz, CDCl₃): δ = 8.28 (d, *J* = 4.80 Hz, 2 H), 8.20 (s, 2 H), 7.79 (d, *J* = 8.40 Hz, 1 H), 7.59 (q, 2 H), 7.48 (m, 3 H), 7.35 (m, 3 H), 7.24 (s, 2 H), 7.10 (t, *J* = 4.50 Hz, 1 H), 4.39 (t, *J* = 7.20 Hz, 2 H), 1.97 (t, *J* = 6.90 Hz, 2 H), 1.56–1.27 (m, 36 H), 0.87 (t, *J* = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 145.51, 142.44, 140.61, 140.31, 139.81, 129.64, 128.01, 126.09, 125.35, 124.88, 123.80, 123.68, 123.50, 123.07, 122.97, 122.14, 119.37, 118.05, 116.20, 109.77, 109.34, 109.19, 43.53, 34.76, 32.09, 31.93, 29.64, 29.55, 29.45, 29.36, 29.13, 27.37, 22.70, 14.13 ppm. FTIR (KBr): \hat{v} = 3047, 2952, 1490, 1362, 1292, 1233, 797 cm⁻¹. HRMS: *m/z* calcd. for C₄₈H₅₈N₂S 694.4321; found 695.4405 [M + H]⁺.

6-(5-Bromothiophen-2-yl)-3-(3',6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazole (5): NBS (0.87 g, 4.98 mmol) was added in small portions to a stirred solution of 4 (3.30 g, 4.75 mmol) in THF (70 mL). The mixture was stirred at room temperature for 3 h. Water (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (50 mL \times 3). The combined organic phase was washed with water (50 mL) and brine (50 mL), dried with anh. Na_2SO_4 and filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel with elution with a mixture of CH₂Cl₂ and hexane (1:3) followed by recrystallization with a mixture of CH_2Cl_2 and methanol afforded the product (3.33 g, 91%) as a green solid (m.p. 174 °C). ¹H NMR (300 MHz, CDCl₃): δ = 8.26 (s, 2 H), 8.21 (s, 2 H), 7.69 (d, J = 8.40 Hz, 3 H), 7.61 (d, J = 6.90 Hz, 3 H), 7.50–7.46 (m, 3 H), 7.35 (d, J = 8.70 Hz, 2 H), 7.08–7.04 (q, 2 H), 4.40 (t, J = 7.20 Hz, 2 H), 1.98 (t, J = 6.90 Hz, 2 H), 1.57–1.27 (m, 36 H), 0.89 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 147.02, 142.48, 140.76, 140.26, 139.81, 130.82, 129.79, 125.50, 125.30, 124.49, 123.54, 123.50, 123.08, 123.00, 122.23, 119.34, 117.80, 116.21, 110.03, 109.85, 109.47, 109.15, 43.55, 34.75, 32.08, 31.92, 29.63, 29.60, 29.53, 29.43, 29.35, 29.10, 27.35, 22.69, 14.12 ppm. FTIR (KBr): v = 3047, 2952, 1490, 1359, 1297, 1230, 808 cm⁻¹. HRMS: *m*/*z* calcd. for C₄₈H₅₇BrN₂S 772.3426; found 773.3482 [M + H]⁺.

6-(2,2'-Bithiophen-5-yl)-3-(3',6'-di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazole (6): Compound 6 (1.35 g, 80%) was synthesized from 5 in similar manner to 4 and obtained as a pale yellow solid (m.p. 142 °C). ¹H NMR (300 MHz, CDCl₃): δ = 8.27 (s, 2 H), 8.20 (s, 2 H), 7.78 (d, J = 8.40 Hz, 1 H), 7.60 (q, 2 H), 7.49–7.46 (m, 3 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.27–7.16 (m, 3 H), 7.03 (t, J =3.9 Hz, 1 H, 4.39 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H),1.50–1.27 (m, 36 H), 0.89 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR $(75 \text{ MHz}, \text{CDCl}_3)$: $\delta = 144.35, 142.46, 140.68, 140.28, 139.81,$ 137.73, 135.62, 129.74, 127.81, 125.71, 125.39, 124.68, 124.50, 124.02, 123.64, 123.50, 123.29, 123.08, 123.03, 122.66, 119.34, 117.73, 116.19, 109.81, 109.41, 109.19, 43.55, 34.75, 32.08, 31.92, 29.63, 29.60, 29.54, 29.43, 29.35, 29.12, 27.36, 22.69, 14.12 ppm. FTIR (KBr): $\tilde{v} = 3047$, 2946, 1490, 1365, 1292, 1233, 791 cm⁻¹. HRMS: m/z calcd. for C₅₂H₆₀N₂S₂ 776.4198; found 777.4290 [M $+ H^{+}_{-}$

6-(5'-Bromo-2,2'-bithiophen-5-yl)-3-(3',6'-di-*tert***-butylcarbazol-***N'***-yl)-***N***-dodecylcarbazole (7):** Compound 7 (0.98 g, 79%) was synthesized from **6** in similar manner to **5** and obtained as a green solid (m.p. 234 °C). ¹H NMR (300 MHz, CDCl₃): δ = 8.24 (s, 2 H), 8.17 (s, 2 H), 7.74 (d, *J* = 5.58 Hz, 1 H), 7.59–7.57 (m, 2 H), 7.47 (d, *J* = 8.60 Hz, 3 H), 7.33 (d, *J* = 8.60 Hz, 3 H), 7.21 (d, *J* = 3.72 Hz, 1 H), 7.10 (d, *J* = 3.72 Hz, 1 H), 6.97–6.90 (q, 2 H), 4.37 (t, *J* = 7.20 Hz, 2 H), 1.98 (t, *J* = 6.90 Hz, 2 H), 1.57–1.27 (m, 36 H), 0.85 (t, *J* = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 144.90, 142.48, 140.75, 140.26, 139.81, 139.22, 134.50, 130.64, 129.78, 23.59, 123.50, 123.30, 123.08, 122.69 48, 109, 85, 109, 45, 109, 17, 43, 55, 34, 75

125.45, 124.95, 124.50, 123.59, 123.50, 123.30, 123.08, 122.69, 119.34, 117.79, 116.21, 110.48, 109.85, 109.45, 109.17, 43.55, 34.75, 32.08, 31.92, 30.92, 29.63, 29.60, 29.54, 29.43, 29.35, 29.11, 27.36, 22.70, 14.12 ppm. FTIR (KBr): $\tilde{v} = 3041$, 2956, 1493, 1363, 1295, 1263, 811 cm⁻¹. HRMS: *m/z* calcd. for C₅₂H₅₉BrN₂S₂ 854.3303; found 855.3364 [M + H]⁺.

5-[3-(3',6'-Di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]thiophene-2-carbaldehyde (8): A mixture of 3 (1.20 g, 1.73 mmol), 5-formylthiophene-2-boronic acid (0.26 g, 1.73 mmol), Pd(PPh₃)₄ (0.05 g, 0.04 mmol) and Na₂CO₃ solution (2 M, 20 mL) in THF (30 mL) was degassed with N2 for 3 min. The mixture was heated at reflux under N2 for 48 h. After the mixture had cooled, water (50 mL) was added, and the mixture was extracted with CH₂Cl₂ (50 mL \times 2). The combined organic phase was washed with water $(50 \text{ mL} \times 2)$ and brine (50 mL), dried with anh. Na₂SO₄ and filtered, and the solvents were removed to dryness. The crude product was purified by silica gel column chromatography with a mixture of CH₂Cl₂ and hexane (1:3) as an eluent followed by recrystallization with a mixture of CH2Cl2 and methanol afforded the product (0.71 g, 57%) as a yellow solid (m.p. 230 °C). ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3): \delta = 9.87 \text{ (s, 1 H)}, 8.37 \text{ (s, 1 H)}, 8.27 \text{ (s, 1 H)},$ 8.19 (s, 2 H), 7.83 (d, J = 8.70 Hz, 1 H), 7.75 (d, J = 3.90 Hz, 1 H), 7.67–7.58 (q, 2 H), 7.51–7.43 (m, 4 H), 7.35 (d, *J* = 8.70 Hz, 2 H), 4.40 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H), 1.57–1.27 (m, 36 H), 0.87 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): *δ* = 182.54, 155.91, 142.58, 141.66, 141.44, 140.22, 139.88, 137.76, 130.19, 125.78, 125.05, 124.52, 123.54, 123.14, 123.00, 119.39, 118.69, 116.24, 110.05, 109.68, 109.12, 43.63, 34.75, 32.07, 31.91, 30.91, 29.71, 29.62, 29.58, 29.52, 29.41, 29.34, 29.09, 27.34, 22.68, 14.10 ppm. FTIR (KBr): $\tilde{v} = 2952$, 1647(C=O), 1495, 1435, 1361, 1295, 1240, 1060, 807 cm⁻¹. HRMS: m/z calcd. for C₄₉H₅₈N₂OS 722.4270; found 723.4365 [M + H]⁺.

5'-[3-(3',6'-Di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]-2,2'-terthiophene-2-carbaldehyde (9): Compound 9 (0.32 g, 63%) was synthesized from 5 in similar manner to 8 and obtained as an orange solid (m.p. > 250 °C). ¹H NMR (300 MHz, CDCl₃): δ = 9.85 (s, 1 H), 8.27 (s, 2 H), 8.20 (s, 2 H), 7.78 (d, J = 7.20 Hz, 1 H), 7.66 (d, J = 3.90 Hz, 1 H), 7.63–7.57 (q, 2 H), 7.50–7.47 (m, 3 H), 7.37–7.35 (m, 3 H), 7.29 (d, J = 3.90 Hz, 1 H), 7.24 (d, J =3.90 Hz, 1 H), 4.39 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H), 1.58–1.27 (m, 36 H), 0.88 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR $(75 \text{ MHz}, \text{CDCl}_3)$: $\delta = 182.40, 147.59, 147.57, 142.53, 141.17,$ 141.01, 140.25, 139.83, 137.49, 133.95, 129.92, 127.32, 125.58, 125.02, 124.55, 123.65, 123.56, 123.52, 123.15, 123.11, 123.08, 119.35, 118.00, 116.24, 109.94, 109.56, 109.15, 43.58, 34.76, 32.09, 31.93, 29.64, 29.60, 29.54, 29.43, 29.36, 29.12, 27.36, 22.70, 14.13, 140.91, 140.50, 140.26, 139.82, 134.79, 130.51, 129.86, 126.21, 125.51, 125.44, 124.54, 1223.61, 123.53, 123.37, 123.11, 123.06, 119.33, 117.93, 116.24, 109.91, 109.50, 109.17, 43.57, 34.77, 32.10, 31.93, 29.64, 29.61, 29.55, 29.44, 29.37, 29.13, 27.37, 22.71, 14.14 ppm. FTIR (KBr): \tilde{v} = 3055, 2956, 1647 (C=O), 1493, 1452, 1363, 1295, 1223, 1047, 807 cm⁻¹. HRMS: m/z calcd. for C₅₃H₆₀N₂OS₂ 804.4147; found 805.4189 [M H]⁺.

5''-**[**3-(3',6'-**D**i-*tert*-butylcarbazol-*N*'-yl)-*N*-dodecylcarbazol-6-yl]-**2**,2':5',2''-terthiophene-2-carbaldehyde (10): Compound 10 (0.66 g, 66%) was synthesized from 7 in similar manner to **9** and obtained as a red orange solid (m.p. > 250 °C). ¹H NMR (300 MHz, CDCl₃): $\delta = 9.85$ (s, 1 H), 8.27 (s, 2 H), 8.21 (s, 2 H), 7.77 (d, J = 8.40 Hz, 1 H), 7.65–7.56 (m, 3 H), 7.50–7.45 (m, 3 H), 7.36 (d, J = 8.40 Hz, 2 H), 7.26–7.20 (m, 4 H), 7.12 (d, J = 3.30 Hz, 1 H), 4.38 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H), 1.57–1.27 (m, 36 H), 0.88 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃):

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$$\begin{split} &\delta = 182.35, 146.97, 145.60, 142.52, 141.45, 140.82, 140.26, 139.81, \\ &139.57, 137.37, 134.46, 134.01, 129.84, 129.84, 127.02, 125.51, \\ &125.34, 124.47, 124.12, 123.90, 123.59, 123.52, 123.11, 123.06, \\ &122.88, 119.32, 117.82, 116.23, 109.88, 109.49, 109.17, 43.56, 34.76, \\ &32.09, 31.93, 29.63, 29.61, 29.54, 29.43, 29.35, 29.12, 27.36, 22.70, \\ &14.13 \text{ ppm. FTIR (KBr): } \tilde{v} = 3055, 2953, 1651 (C=O), 1491, 1453, \\ &1362, 1295, 1231, 1047, 807 \text{ cm}^{-1}. \text{ HRMS: } m/z \text{ calcd. for } \\ &C_{57}H_{62}N_2OS_3, 886.4024; \text{ found } 887.4091 [M + H]^+. \end{split}$$

4-{5'-[3-(3',6'-Di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]-2,2'-bithiophen-5-yl}benzaldehyde (11): Compound 11 (0.89 g, 91%) was synthesized from 7 and 4-formylphenylboronic acid in similar manner to 9 and obtained as a yellow solid (m.p. > 250 °C). ¹H NMR (300 MHz, CDCl₃): δ = 9.99 (s, 1 H), 8.27 (s, 2 H), 8.21 (s, 2 H), 7.88 (d, J = 8.10 Hz, 2 H), 7.79–7.72 (m, 3 H), 7.65–7.56 (q, 2 H), 7.50–7.46 (m, 3 H), 7.38–7.35 (m, 3 H), 7.21 (d, J = 3.60 Hz, 3 H), 4.39 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H), 1.57-1.27 (m, 36 H), 0.88 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, $CDCl_3$): $\delta = 191.30, 145.25, 142.51, 140.79, 140.66, 140.27, 139.82,$ 139.35, 134.98, 130.49, 129.83, 125.92, 125.56, 125.46, 125.24, 124.48, 124.38, 123.61, 123.51, 123.11, 123.06, 122.85, 119.33, 117.81, 116.22, 109.87, 109.48, 109.18, 43.56, 34.76, 32.08, 31.92, 29.63, 29.60, 29.54, 29.43, 29.35, 29.12, 27.36, 22.69, 14.11 ppm. FTIR (KBr): $\tilde{v} = 3064, 2952, 1692$ (C=O), 1602, 1490, 1454, 1359, 1261, 1211, 791 cm⁻¹. HRMS: m/z calcd. for C₅₉H₆₄N₂OS₂ 880.4460; found 881.3466 [M + H]⁺.

(E)-3-{2-[3-(3',6'-Di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6yl]thiophen-5-yl}-2-cyanoacrylic Acid (CCT1A): Piperidine (0.14 mL) was added to a mixture of 8 (0.41 g, 0.55 mmol) and 2cyanoacetic acid (0.09 g, 1.12 mmol) in CHCl₃ (20 mL). The solution was heated at reflux overnight. The solvent was removed to dryness. Purification by column chromatography over silica gel with elution with a mixture of CH_2Cl_2 and hexane (4:1) followed by recrystallization with a mixture of CH2Cl2 and methanol afforded the product (0.25 g, 57%) as a red-orange solid (m.p. 176 °C). ¹H NMR (300 MHz, $[D_6]DMSO/CDCl_3$): $\delta = 8.40$ (s, 1 H), 8.30 (d, J = 7.45 Hz, 2 H), 8.20 (s, 2 H), 7.90 (d, J = 8.59 Hz, 1 H), 7.80 (d, J = 8.61 Hz, 1 H), 7.60 (q, 2 H) 7.50 (q, 4 H), 7.40 (d, 2 H) 4.39 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H), 1.57-1.27 (m, 36 H), 0.87 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, $[D_6]DMSO/CDCl_3$: $\delta = 164.18, 151.97, 142.55, 141.50, 139.90,$ 138.03, 135.10, 131.94, 129.61, 129.08, 125.41, 125.08, 124.61, 123.99, 123.58, 123.01, 119.80, 119.21, 119.04, 116.90, 111.22, 110.81, 109.52, 105.73, 43.15, 34.91, 34.17, 32.31, 31.71, 29.42, 29.29, 29.12, 28.99, 26.84, 24.96, 22.50, 14.32 ppm. FTIR (KBr): v = 3413 (O–H), 3047, 2923, 2211 (C≡N), 1604 (C=O), 1490, 1363, 1294, 1262, 801 cm⁻¹. HRMS: m/z calcd. for C₅₂H₅₉N₃O₂S 789.4328; found 789.4462 [M]+.

(*E*)-3-{5'-[3-(3',6'-Di-*tert*-butylcarbazol-*N*'-yl)-*N*-dodecylcarbazol-6-yl]-2,2'-bithiophen-5-yl}-2-cyanoacrylic Acid (CCT2A): Compound CCT2A (0.27 g, 60%) was synthesized from 9 in similar manner to CCT1A and obtained as a red solid (m.p. 250 °C). ¹H NMR (300 MHz, [D₆]DMSO/CDCl₃): δ = 8.50 (s, 1 H), 8.40 (s, 1 H), 8.15 (s, 2 H), 8.10 (s, 2 H), 7.75 (t, 2 H), 7.60 (q, 3 H), 7.40 (d, *J* = 5.40 Hz, 4 H), 7.3 (t, 2 H) 4.39 (t, *J* = 7.20 Hz, 2 H), 1.97 (t, *J* = 6.90 Hz, 2 H), 1.57–1.27 (m, 36 H), 0.87 (t, *J* = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO/CDCl₃): δ = 163.47, 145.98, 142.56, 141.85, 140.99, 140.24, 139.92, 139.84, 136.36, 135.93, 133.92, 129.44, 127.09, 125.21, 124.91, 124.50, 124.16, 123.96, 119.74, 119.60, 118.45, 116.75, 111.04, 110.61, 110.05, 109.53, 43.16, 34.87, 32.29, 31.71, 29.40, 29.27, 29.11, 28.96, 26.84, 22.50, 14.30 ppm. FTIR (KBr): \tilde{v} = 3417 (O–H), 3047, 2925, 2211 (C=N), 1609 (C=O), 1490, 1363, 1295, 1152, 801 cm⁻¹. HRMS: m/z calcd. for C₅₆H₆₁N₃O₂S₂ 871.4205; found 872.4288 [M + H]⁺.

(*E*)-3-{5''-[3-(3',6'-Di-*tert*-butylcarbazol-*N*'-yl)-*N*-dodecylcarbazol-6-yl]-2,2':5',2''-terthiophen-5-yl}-2-cyanoacrylic Acid (CCT3A): Compound CCT3A (0.19 g, 67%) was synthesized from 10 in similar manner to CCT1A and obtained as a dark red solid (m.p. > 250 °C). ¹H NMR (300 MHz, [D₆]DMSO/CDCl₃): δ = 8.56 (s, 1 H), 8.47 (s, 1 H), 8.22 (s, 3 H), 7.98–7.79 (m, 4 H) 7.67–7.58 (m, 3 H), 7.45–7.27 (m, 7 H), 4.48–4.45 (m, 2 H), 2.06–1.83 (m, 2 H), 1.40–1.15 (m, 36 H), 0.77 (s, 3 H) ppm. ¹³C NMR (75 MHz, [D₆]-DMSO/CDCl₃): δ = 162.89, 142.59, 140.93, 139.96, 137.63, 136.48, 134.05, 129.41, 126.97, 126.28, 125.13, 124.80, 124.02, 123.90, 123.53, 122.96, 119.76, 116.81, 111.13, 110.66, 109.54, 43.19, 36.30, 34.90, 32.31, 31.71, 31.28, 29.40, 29.26, 29.10, 28.96, 27.57, 26.84, 22.50, 14.32 ppm. FTIR (KBr): \tilde{v} = 3417 (O–H), 2937, 2213 (C=N), 1610 (C=O), 1490, 1365, 1295, 1262, 808 cm⁻¹. HRMS: *m*/*z* calcd. for C₆₀H₆₃N₃O₂S₃ 953.4082; found 953.4265 [M]⁺.

(E)-3-(4-{5'-[3-(3',6'-Di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]-2,2'-bithiophen-5-yl}phenyl)-2-cyanoacrylic Acid (CCT2PA): Compound CCT2PA was synthesized from 11 in similar manner to CCT1A and obtained as a red solid (0.15 g, 96%), m.p. > 250 °C. ¹H NMR (300 MHz, $[D_6]DMSO/CDCl_3$): $\delta = 8.72$ (s, 2 H), 8.45 (s, 2 H), 8.27 (s, 3 H), 8.17 (s, 2 H), 7.79-7.56 (m, 8 H), 7.41 (d, J = 8.40 Hz, 2 H), 7.25 (d, J = 8.40 Hz, 2 H), 4.42 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H), 1.57–1.27 (m, 36 H), 0.87 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO/ $CDCl_3$): $\delta = 166.30, 142.43, 139.97, 139.86, 134.70, 130.61, 129.44,$ 125.22, 124.36, 123.73, 1223.84, 123.73, 1223.48, 122.88, 119.16, 117.64, 116.21, 110.37, 109.38, 43.28, 34.74, 32.17, 31.80, 30.95, 29.51, 29.45, 29.28, 29.22, 22.58, 14.24 ppm. FTIR (KBr): $\tilde{v} = 3416$ (O-H), 3047, 2924, 2214 (C≡N), 1598 (C=O), 1491, 1363, 1293, 1148, 792 cm⁻¹. HRMS: m/z calcd. for $C_{62}H_{65}N_3O_2S_2$ 947.4518; found 947.4775 [M]+.

(E)-3-{5''-[3-(3',6'-Di-tert-butylcarbazol-N'-yl)-N-dodecylcarbazol-6-yl]-2,2':5',2''-terthiophen-5-yl}-2-cyanoacrylamide (CCT3N): A mixture of 10 (0.30 g, 0.34 mmol), 2-cyanoacetamide (0.04 g, 0.51 mmol) and NH₄OAc (0.13 g, 1.69 mmol) was dissolved in AcOH (25 mL), CH₃CN (20 mL) and THF (20 mL). The solution was heated at reflux overnight. After the mixture had cooled, water (50 mL) was added, and the mixture was extracted with CH₂Cl₂ (50 mL \times 2). The combined organic phase was washed with water (50 mL \times 2) and brine (100 mL), dried with anh. Na₂SO₄ and filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel with elution with CH2Cl2 followed by recrystallization with a mixture of CH2Cl2 and methanol afforded the product (0.22 g, 70%) as a red solid (m.p. > 250 °C). ¹H NMR (300 MHz,CDCl₃): δ = 8.31 (s, 1 H), 8.26 (s, 2 H), 8.19 (s, 2 H), 7.75 (d, J = 7.80 Hz, 1 H), 7.61–7.55 (q, 3 H), 7.49–7.47 (m, 3 H), 7.35 (d, J = 8.40 Hz, 2 H), 7.26–7.12 (m, 5 H), 6.20 (s, 1 H), 5.75 (s, 1 H), 4.39 (t, J = 7.20 Hz, 2 H), 1.97 (t, J = 6.90 Hz, 2 H), 1.71–1.28 (m, 36 H), 0.89 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 162.36, 146.72, 145.76, 145.14, 142.52, 140.85, 140.27, 139.90, 139.82, 138.91, 134.44, 134.27, 133.75, 129.88, 127.28, 125.61, 125.49, 125.33, 124.48, 124.25, 124.12, 123.61, 123.50, 123.11, 123.03, 122.93, 119.32, 117.83, 117.42, 116.20, 109.87, 109.48, 109.17, 43.56, 34.74, 32.06, 31.90, 30.86, 29.60, 29.57, 29.51, 29.40, 29.32, 29.09, 27.34, 22.66, 14.07 ppm. FTIR (KBr): $\tilde{v} = 3442$ (N–H), 3053, 2924, 2218 (C=N), 1596 (C=O), 1491, 1363, 1294, 1187, 794 cm⁻¹. HRMS: *m/z* calcd. for $C_{60}H_{64}N_4OS_3$ 952.4242; found 953.4238 [M + H]⁺.

Supporting Information (see footnote on the first page of this article): PL spectra, TGA and DPV curves, more quantum chemical

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Organic Dyes for Efficient Dye-Sensitized Solar Cells

results, FTIR spectra of dyes adsorbed on TiO_2 , and ¹H and ¹³C NMR spectra of the dyes and intermediates.

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