Synthesis of innovative triphenylamine-functionalized organic photosensitizers outperformed the benchmark dye N719 for high-efficiency dye-sensitized solar cells

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Herein, we present a thorough photovoltaic investigation of four triphenylamine organic sensitizers with D–π–A configurations and compare their photovoltaic performances to the conventional ruthenium-based sensitizer N719. SFA-5–8 are synthesized and utilized as sensitizers for dye-sensitized solar cell (DSSC) applications. The effects of the donor unit (triphenylamine), π-conjugation bridge (thiophene ring), and various acceptors (phenylacetonitrile and 2-cyanoacetamide derivatives) were investigated. Moreover, this was asserted by profound calculations of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels, the molecular electrostatic potential (MEP), and natural bond orbital (NBO) that had been studied for the TPA-sensitizers. Theoretical density functional theory (DFT) was performed to study the distribution of electron density between donor and acceptor moieties. The sensitization by the absorption of sensitizers SFA-5–8 leads to an obvious enhancement in the visible light absorption (300–750 nm) as well as a higher photovoltaic efficiency in the range of (5.53–7.56%). Under optimized conditions, SFA-7 showed outstanding sensitization of nanocrystalline TiO2, resulting in enhancing the visible light absorption and upgrading the power conversion efficiency (PCE) to approximately 7.56% over that reported for the N719 (7.29%). Remarkably, SFA-7 outperformed N719 by 4% in the total conversion efficiency. Significantly, the superior performance of SFA-7 could be mainly ascribed to the higher short-circuit photocurrents ($J_{sc}$) in parallel with larger open-circuit voltages ($V_{oc}$) and more importantly, the presence of different anchoring moieties that could enhance the ability to fill the gaps on the surface of the TiO2 semiconductor. That could be largely reflected in the overall enhancement in the device efficiency. Moreover, the theoretical electronic and photovoltaic properties of all studied sensitizers have been compared with experimental results. All the 2-cyanoacrylamide derivative sensitizers demonstrated robust photovoltaic performance.

In the unprecedented dilemma of the ever-growing shortage of energy resources and compelling energy demands, dye-sensitizers are considered the holy grail of renewables and the core of dye-sensitized solar cells (DSSCs) because of their availability and pollution-free nature. In 1991, O’Regan and Graetzel described a novel type of sensitizer known as DSSCs. They have become promising alternatives to traditional silicon-based photovoltaics because they are cheap, work well, and are easy to make. New attempts have been proposed to present new approaches for the development of dye sensitizers. Most of such dyes are based on metal–organic complexes like ruthenium (Ru) dye sensitizers that are widely used due to their wide optical absorption, high photostability, and energy compatibility with the TiO2 layer. This in turn could achieve high DSSC performance associated with various anchoring carboxylate groups via the metal-to-ligand charge transfer (MLCT) processes. Despite the high efficiencies of the sensitized devices with ruthenium-based dyes such as N3, N719, black dye, and HD-2,
they pose many issues in terms of their high cost, scarcity of metal, and highly purified methods. In this regard, metal-free organic sensitizers could be a good choice. There are various types of metal-free sensitizers such as carbazole, phenothiazine, coumarin, thiophene, triphenylamine, and boron dipyrromethene (BODIPY) with classifications D–π–A, D–D–π–A, and D–π–A–A. In comparison to their metal-based counterparts, such as porphyrin dye and chlorophyll-based dyes, they all have a high molar extinction coefficient, low cost, and ease of purification. Metal-free sensitizers have been widely recognized to have a complementary absorption profile with a high molar extinction coefficient and higher efficiencies. Amongst donor units, triphenylamine, phenothiazine, carbazole, and coumarin have been commonly utilized as promising metal-free sensitizers. In this context, TPA sensitizers are characterized by their higher stability, electron-donating capacity, and aggregation resistance, which render them suitable candidates for DSSC applications.

Generally, TPA-based sensitizers can reduce aggregation and allow the interfacial electron injection of excited dye molecules into the TiO2 conduction band. Furthermore, TPA compounds can inhibit charge carriers’ recombination of the redox couple (I3−/I−) due to their propeller-shaped molecular structure. Such remarkable properties of organic sensitizers are directly related to structure variations, small sizes, and, most importantly, photovoltaic properties. As previously stated, our research team was interested in developing and introducing new co-sensitizers based on D–π–A cyanocacetanilide compounds with multimolecular structures and a variety of acceptor and donor moieties. Furthermore, an ideal sanitizer should have specific functional groups called anchoring groups to enable strong binding between the dye and the surface of the semiconductor oxide. Historically, the most frequently used anchors in DSSCs are carboxylic acid and cyanocarboxylic acid groups. The anchoring groups link with the TiO2 surface to enable the injection of the excited electron into the CB of the TiO2.

Due to the exponential growth of DSSC research in recent years, many new anchors have been made and tested. This has greatly increased the number of materials available and made it easier to understand DSSCs. Against this background, we present the design, synthesis, characterization, and photovoltaic performance of four innovative sensitizers stated as SFA-5–8, containing a triphenylamine moiety as a donor group attached to π-bridge (thiophene moiety) linked to different 2-cyano-acrylamide acceptors and phenyl acetonitrile units. Such D–π–A SFA-5–8 models have been schematically represented in Fig. 1. In addition, 2-cyano-acrylamide and phenyl acetonitrile units containing electron-withdrawing groups (EWGs) as CN, CO, NO2, and amide (CONH) are of great importance in organic synthesis due to their strong accepting ability. Hence, 2-cyano-acrylamide acceptor and phenyl acetonitrile units were chosen because they possess the good electron-accepting ability and,

![Figure 1. Molecular structures of sensitizers SFA-5–8 and N719.](image-url)
3-(5-(4-Diphenylamino)styryl)thiophene-2-yI thiophene-2-carbaldehyde (6). Thiophene-2-carbaldehyde compound 6 has been synthesized through two reactions, firstly phosphonium salt and 2-formylthiophene react via Wittig reaction under alkaline conditions (t-BuOK). At 50 mL two-neck RB flask, 19 mL of freshly distilled POCl₃ was added dropwise to the (20 mL) of a stirred solution of dry DMF at 0 °C under argon atmosphere until colored Vilsmeier salt completely precipitates. Then a solution of 5 (0.54 g of N,N-diphenyl-4-(2-(thiophene-2-yl)vinyl) aniline dissolved in 10 mL DMF) was added to the reaction mixture drop by drop with continuous stirring for 1 h. The temperature was increased to 120 °C for 2 h, then the mixture was stirred overnight at room temperature. After completion of the reaction, the mixture was poured into 100 mL of ice-cold water and the pH was adjusted to alkaline by adding saturated sodium acetate solution. The solid product was collected by filtration and washed with water. After drying, the precipitate was purified by recrystallization from a mixture of ethanol (50 mL) and drops of acetic acid. Yield = 69%, m.p. = 172–174 °C. IR (KBr): νₘₐₓ 3334 (N–H), 2209 (C≡N), 1675 cm⁻¹ (C=O). ¹H NMR (DMSO-d₆): δ 7.90–8.14 (m, 11H, Ar–H), 8.21 (d, J = 4.00 Hz, 1H, thiophene-H), 8.24 (d, J = 8.00 Hz, 2H, Ar–H), 8.46 (d, J = 4.00 Hz, 1H, thiophene-H), 8.49 (d, J = 8.00 Hz, 2H, Ar–H), 8.93 (s, 1H, C=CH) ppm. ¹³C NMR (DMSO-d₆): δ 111.32, 119.61, 120.75, 121.49, 124.63 (2C), 126.71, 127.10, 127.49, 127.76 (2C), 128.39 (4C), 129.39 (2C), 130.15, 130.33 (4C), 134.70 (2C), 143.47 (4C), 147.29, 148.22, 149.22, 150.29 (2C), 155.78, 156.04, 160.54 ppm. Analysis calcd. for C₃₄H₂₄N₄O₃S (568.16): C, 71.81; H, 4.25; N, 9.95%. Found: C, 71.76; H, 4.18; N, 9.95%.

2-Cyano-3-(5-(4-Diphenylamino)styryl)thiophene-2-yl-N-(4-nitrophenyl)acrylamide (SFA-6). 5-(4-Diphenylamino)styryl thiophene-2-carbaldehyde (6) (0.76 g, 2 mmol) and 2-cyano-N-(4-nitrophenyl)acetamide (0.41 g, 2 mmol) were dissolved in methanol (15 mL). Acetic acid (0.20 mL) was added to the mixture, reflux was continued for 18 h and then cooled to room temperature. The solid that obtained was purified using silicone gel column chromatography to obtain dark brown solid compound. Yield = 88%, m.p. = 190–192 °C. IR (KBr): νₘₐₓ 3330 (N–H), 2222 (C≡N), 1675 cm⁻¹ (C=O). ¹H NMR (DMSO-d₆): δ 8.00 (2H, Ar–H), 8.14 (d, J = 4.00 Hz, 1H, Ar–H), 8.18 (d, J = 4.00 Hz, 1H, thiophene-H), 8.21 (d, J = 4.00 Hz, 1H, thiophene-H), 8.24 (d, J = 8.00 Hz, 2H, Ar–H), 8.29 (d, J = 8.00 Hz, 1H, Ar–H), 8.46 (d, J = 4.00 Hz, 1H, thiophene-H), 8.49 (d, J = 8.00 Hz, 2H, Ar–H), 8.90–8.93 (s, 1H, C=CH) ppm. ¹³C NMR (DMSO-d₆): δ 111.32, 119.61, 120.75, 121.49, 124.63 (2C), 126.71, 127.10, 127.49, 127.76 (2C), 128.39 (4C), 129.39 (2C), 130.15, 130.33 (4C), 134.70 (4C), 143.47 (4C), 147.29, 148.22, 149.22, 150.29 (2C), 155.78, 156.04, 160.54 ppm. Analysis calcd. for C₃₅H₂₃N₄O₅S (586.16): C, 71.81; H, 4.25; N, 9.95%. Found: C, 71.76; H, 4.18; N, 9.95%.
2-Cyano-3-(5-(4-(diphenylamino) styryl)thiophen-2-yl)-N-(pyridin-4-yl)acrylamide (SFA-8). To a suspension of 6 (0.76 g, 2 mmol) and 2-cyano-N-(pyridin-4-yl)acetamide (7d) (0.32 g, 2 mmol) in 15 mL ethanol, 0.2 mL piperidine has been added. The reaction mixture was refluxed for 10 h and the pure sensitizer SFA-8 was separated by filtration after cooling the solution to room temperature for obtaining dark brown crystals. Yield = 80%, m.p. = 184–186 °C. IR (KBr): νmax 3324 (N–H), 2219 (C≡N), 1679 (C=O) cm⁻¹. 1H NMR (DMSO-d6): δ 6.95 (d, J = 12.00 Hz, 1H, C=CH), 7.74 (d, J = 12, 1H, C = CH), 7.90 (t, J = 6.00 Hz, 2H, Ar–H), 8.07 (t, J = 8.00 Hz, 4H, Ar–H), 8.11–8.14 (m, 5 H, Ar–H and thiophene-H), 8.07 (t, J = 8.00 Hz, 2H, Ar–H), 8.20 (s, 1H, C=CH), 8.40 (s, 1H, C=CH), 8.46 (d, J = 4.00 Hz, 1H, thiophene-H), 8.49 (d, J = 4.00 Hz, 2H, pyridine-H), 8.92 (d, J = 4.00 Hz, 2H, pyridine-H). 13C NMR (DMSO-d6): δ 110.93 (2C), 119.35, 121.15, 126.05 (2C), 126.66, 127.19 (4C), 127.40 (2C), 128.05 (4C), 128.09, 128.16, 128.35, 128.47, 132.37, 132.71, 134.00, 134.09 (2C), 143.30, 146.12, 148.23 (2C), 154.76, 155.76, 155.14, 155.95, 168.04 ppm. Analysis calcd. for C35H25N3O3S (567.16): C, 74.06; H, 4.44; N, 7.40%. Found: C, 74.26; H, 4.52; N, 7.53%.

Results and discussion.  
Synthesis and structure characterization. The synthetic pathways of four new triphenylamine-based organic compounds (SFA-5–8) are depicted in Figs. 2 and 3. Figure 2 shows the synthetic pathway of 5-(4-(diphenylamino) styryl)thiophene-2-carbaldehyde (6), including the reaction of 4-((bromotriphenyl-λ5-phosphanyl)methyl)-N,N-diphenylaniline (3) with 2-formylthiophene (4) under Wittig reaction conditions, obtaining the corresponding thiophene bridge (5). The intermediate 5 was then formulated using the standard Vilsmeier-Hack reaction protocol to yield 5-(4-(diphenylamino) styryl)thiophene-2-carbaldehyde (6) with a good overall yield (Fig. 2). The observed melting point and spectroscopic characterization of triphenyl amine-based compounds 5 and 6 were well-matched with previous studies. Afterward, 2-cyanoacetamide derivatives 7b–d were synthesized in a high yield via the refluxing of various aromatic amines such as 4-nitro aniline, 4-aminobenzoic acid, and 4-aminopyridine with 1-cyanoacetyl-3,5-dimethylpyrazole in dioxane as a solvent, as previously stated in the literature. Finally, the targeted final products SFA-5–8 were formed in a high yield through Knoevenagel condensation of 5-(4-(diphenylamino) styryl) thiophene-2-carbaldehyde (6) with 2-(4-nitrophenyl)acetanitrile (7a) and three 2-cyanoacetamide derivatives 7b, 7c and 7d as shown in Fig. 3. The end products SFA-5–8, as well as their intermediates, were extensively purified using column chromatography in addition to the recrystallization process. The structures of the newly synthesized sensitizers and their intermediates were confirmed by various spectroscopic techniques. According to their spectral analysis and elemental investigation, the molecular structure of SFA-5–8 was determined. The IR spectrum of compound SFA-5 revealed characteristic absorption bands of groups, C–H aliphatic at 2922 and 2854 cm⁻¹, and cyano group (C≡N) at 2209 cm⁻¹. Moreover, the stretching vibration band of vinyl groups (C=C) appeared at 1612 cm⁻¹. Its corresponding 1H NMR spectrum exhibited a doublet signal at δ 6.97 ppm that could be attributed to the two protons of the vinylic group with (J = 12.00 Hz), singlet for the olefinic proton at δ 7.94 ppm. The aromatic and thiophene protons resonate as multiplet, triplet, and doublet signals at (δ 7.20–8.15 ppm). Additionally, the IR spectrum of compound SFA-6 exhibited stretching vibration bands at 3330 cm⁻¹ and 2222 cm⁻¹ due to the N–H and C≡N moieties, respectively. Moreover, a strong band at 1675 cm⁻¹ has been detected that could be assigned to the C=O group. The visual inspection of the corresponding 1H NMR
Spectral data revealed a singlet peak at 8.93 ppm corresponding to vinylic proton. Further, the IR spectrum of SFA-7 indicated a vibration band of (C≡N) group at 2220 cm⁻¹ as well as a strong vibration band at 1722 cm⁻¹ attributed to C=O (COOH). Meanwhile, the ¹H NMR spectrum of SFA-7 showed a singlet signal at 13.67 ppm associated with the carboxylic group proton. On the other hand, the ¹³C NMR spectra revealed a characteristic signal at δ 169.00 ppm which could be linked to the carbon of the COOH group. Finally, the IR spectrum of SFA-8 reported absorption bands at 2219 cm⁻¹ and 1679 cm⁻¹ that can be properly assigned to the stretching vibration modes of (C≡N) and (C = O) groups, respectively. Additionally, the ¹³C NMR spectra revealed a characteristic signal at δ 168.04 ppm, ascribable to the carbon of the carbonyl group.

**Optical properties.** The absorption spectra of all synthesize SFA-5–8 sensitizers have been recorded in tetrahydrofuran (THF) solution. Their corresponding data are summarized in Table 1.

| Sensitizer | λMax (nm) | ε (10⁴ M⁻¹ cm⁻¹) | λOnset/nm | Experimental E₀–0 (eV) |
|-----------|-----------|------------------|-----------|---------------------|
| SFA-5     | 256, 354, 468 | 3.20, 0.84, 1.77 | 541       | 2.29                |
| SFA-6     | 254, 356, 481 | 3.81, 0.97, 2.32 | 580       | 2.13                |
| SFA-7     | 253, 345, 478 | 3.78, 1.88, 2.22 | 562       | 2.20                |
| SFA-8     | 255, 342, 474 | 3.11, 1.02, 1.95 | 554       | 2.23                |

Figure 3. Synthetic routes of SFA-5–8 sensitizers.

Table 1. UV–Vis absorption spectra of the synthesized SFA-5–8 sensitizers.
all synthesized sensitizers followed the order of SFA-5 < SFA-8 < SFA-7 < SFA-6. That could be linked to the addition of the π-bridge thiophene group to the SFA-5–8 sensitizers that significantly contributed to energy delocalization and larger polarizability, thus enhancing the visible light absorption. Moreover, the estimated energy gap (E<sub>0-0</sub>), which was calculated from the beginning of the UV–visible absorption spectrum, has been minimized with the presence of the π-bridge linkage, which promoted visible light absorption. Those values followed the order of SFA-6 < SFA-7 < SFA-8 < SFA-5. Importantly, the λ<sub>max</sub> of SFA-5–8 in the visible region appears at 468, 481, 478, and 474 nm, respectively. As expected, electronic density variations between the donating electron and the withdrawing part could imply a bathochromic shift in the internal charge transfer (ICT) band, thus reporting molar extinction coefficients (ε) of approximately 1.77 × 10⁴ mol⁻¹ cm⁻¹, 2.32 × 10⁴ mol⁻¹ cm⁻¹, 2.22 × 10⁴ mol⁻¹ cm⁻¹, and 1.95 × 10⁴ mol⁻¹ cm⁻¹ for SFA-5–8, respectively, associated with their lowest energy bands. Those mentioned values are significantly higher than those reported for the Ru N719 dyes, indicating better light-harvesting ability. For comparison, the UV–Vis absorption spectrum of N719 has been reported in Fig. S1 in the "Supplementary file". Further insights showed that SFA-6–8 was more red-shifted in contrast to its corresponding mono-anchoring SFA-5 dye. This can be attributed to the extension of conjugation length within the synthesized SFA-6-8 molecules, as well as the delocalization across the entire molecule, which could be caused by the addition of an additional anchoring moiety, over 2-cyanoacetamide derivatives. In practical, SFA-6 comprises 4-nitrocyanoacetamide bearing CN, NO₂, and CO substitutions that are mainly responsible for the bathochromic shift with the highest ε value of approximately 2.32 × 10⁴ mol⁻¹ cm⁻¹ amongst all studied dyes, as displayed in Fig. 4. That could be ascribed to the presence of the strongly withdrawing (–NO₂) moiety in their anchoring function. Furthermore, it could be deduced that SFA-7 has more bathochromic shift by around 4 nm, compared to its SFA-8 counterpart, which is associated with its higher degree of conjugation.

Figure 5 shows the absorption spectra of triphenylamine sensitizers SFA-5–8 anchored on the TiO₂ surface. As could be observed, all SFA-5–8 sensitizers showed broadening and blue shifting in the absorption spectra compared to their corresponding spectra recorded in the solution spectrum (250–550 nm). This hypochromic shift is directly related to H-aggregation and strong interaction between the anchoring groups of sensitizers and the semiconductor photoelectrode, which is highly desirable for achieving efficient light-harvesting and promoting the overall efficiency of sensitizers. In particular, it should be emphasized that the observed spectral broadening...
for SFA-7 could be extensively beneficial for enhancing the visible light-harvesting ability and enhancing the short circuit current ($J_{sc}$). The highest absorbance values exhibited by the SFA-7 sensitizer compared to other sensitizers can be mainly ascribed to the deprotonating of carboxylic acid or the formation of H-aggregates on the TiO$_2$ surface, which lead to lowering the $\pi^*$ energy level of its 4-carboxylcyanacetamide group and thereby broadening its absorption spectrum. That in turn could confirm the good ability of the 4-carboxylcyanacetamide of the SFA-7 sensitizer to harvest more photons compared to that of the N719 counterpart. Contrarily, SFA-5 showed the weakest absorbance characteristics compared to other 2-cyanoacetamide derivatives of SFA-6–8 sensitizers, thus confirming the direct effect of anchoring and acceptor groups on the absorbance enhancement. Thereby, we believe that including extra anchoring groups in the design of sensitizers could in turn promote the dye adsorption on the TiO$_2$ surface, narrow the spectrum, and most importantly facilitate the electron flow from the excited dyes to the TiO$_2$ conduction band.$^{36}$

Theoretical calculations. Computational studies for SAF-5–8 dyes were established to unravel how the characteristic $\pi$-spacer and different anchoring/acceptors moiety thru phenylacetonitrile and cyanacetamide derivative sensitizers influence the geometry of the targeted dyes and their DSSC photovoltaic efficiency. The details of the calculations are based on Gaussian 09 software$^{37}$ via B3LYP/6-311 g (d, p) sets$^{38}$. As demonstrated in Fig. 6, the optimized geometrical structures of the SFA-5–8 have been reported. Moreover, their corresponding dihedral angles and bond lengths have been summarized in Table 2. All SFA-5–8 dyes show a propeller starburst arrangement and (D–$\pi$) dihedral angles of about (-179, 179, -177, and 179) with $\pi$-bridges that could be of great importance for achieving efficient charge transfer.

Note that inserting the thiophene moiety is advantageous for increasing the conjugation degree of the SFA-5–8 sensitizers. Meanwhile, DFT calculations showed that SFA-5–8 structures possessed higher dihedral angles that are close to 180° or equal to zero. Such values could reflect better coplanarity configurations and favorable conjugation between the thiophene-$\pi$-spacer and the acceptor moiety.$^{38}$ Indeed, those findings could infer the highest $\lambda_{max}$ values of the SAF-5–8 structures which is a good indicator of the fast electron transfer to the semiconductor surface, resulting in boosting the overall performance. For further insights, Table 2 indicated the bond lengths of

![Figure 6. Illustration of the optimized SFA-5–8 dye sensitizer structures.](image-url)
Different electron acceptors over SFA-5–8 structures. The conjugation impact that could strongly stimulate the electron transfer from the donating TPA moieties to the filled orbitals can be estimated as the following equation:

$$E(2) = \Delta E_{ij} = q_i F(i, j)^2 / \varepsilon_i - \varepsilon_j$$

where $q_i$ represents the donor orbital occupancy, $\varepsilon_i$ and $\varepsilon_j$ the diagonal elements and $F(i, j)$ the off-diagonal. In NBO studies, strong intermolecular hyper conjugative interactions were analyzed by the second-order perturbation theory of the Fock matrix. For SFA-5–8 sensitizers, the higher energy values of $E(2)$ hyper conjugative interactions, the more intensive interaction between an electron donor (TPA moiety) and electron acceptors (NO$_2$, COOH, CN, and pyridyl ring), means the greater ability to donate tendency. Hence the dye aggregation ($\pi-\pi$) as a significant potential to avoid unfavorable dye aggregation ($\pi-\pi$). It is well documented that the dye aggregation mainly contributes to the self-quenching of the electron injection. Therefore, even the dye molecules’ structural geometry gave a valuable foresight about the perceptions of their improved photovoltaic performances as reference. All of these computed findings revealed a strong substantial conjugation impact that could strongly stimulate the electron transfer from the donating TPA moieties to the different electron acceptors over SFA-5–8 structures.

Natural bond orbital analysis. To further elucidate the origin of the intramolecular interactions and give deep insights into the intramolecular electron transfer processes within the synthesized SFA-5–8 sensitizers, NBO analysis could be of crucial importance. In this context, NBO analysis could study the stabilizing interactions between the filled (donor) and empty (acceptor) orbitals as well as the destabilizing interactions between the filled orbitals. By using the second-order perturbation approach, the hyper conjugative interaction energy was estimated from a donor (i), an acceptor (j), and the stabilization energy $E(2)$ associated with the delocalization $j, i$ could be estimated as the following equation:

$$E(2) = \Delta E_{ij} = q_i F(i, j)^2 / \varepsilon_i - \varepsilon_j$$

Quantum chemical parameter SFA-5–8.

The chemical reactivity of the SFA-5–8 sensitizers could be analyzed by utilizing the quantum analysis by calculating several significant factors; including the bandgap energy ($E_{g,a}$), ionization energy (IP), electron affinity (EA), hardness ($\eta$), and softness (s), respectively. With respect Koopmans’ hypothesis framework, the corresponding data are displayed in Table 3.

$$IP = -E_{\text{HOMO}}$$  \hspace{1cm} (2)

$$EA = -E_{\text{LUMO}}$$  \hspace{1cm} (3)

$$\eta = \left( \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \right)$$  \hspace{1cm} (4)

The HOMO–LUMO energy gaps of the SFA-5–8 decreased in a sequence of SFA-7 < SFA-8 < SFA-6 < SFA-5. The smallest $E_{g,a}$ of the SFA-7 structure could reveal its highest stability and confirm its reactive configuration amongst all studied sensitizers, thus allowing for more dominant excitation between the HOMO and LUMO of the SFA-7 dye molecule. Accordingly, 4-carboxycyanoacetamide SFA-7 sensitizer should be chemically more reactive than other SFA-5, SFA-6, and SFA-8 dyes. On the other hand, hardness ($\eta$) and softness (s) are very

| Dye   | HOMO  | LUMO  | $E_{g,a}$ | IP   | EA(s) | $\eta$ | $\Delta G_{inj}$ (eV) | $\Delta G_{req}$ (eV) | $\Delta G_{rec}$ (eV) |
|-------|-------|-------|-----------|------|-------|--------|-----------------------|-----------------------|-----------------------|
| SFA-5 | −5.96 | −3.69 | 2.27      | 5.96 | 3.69  | 0.88   | 1.13                  | −0.51                 | 0.76                  | 1.76                  |
| SFA-6 | −5.70 | −3.50 | 2.20      | 5.70 | 3.50  | 0.90   | 1.10                  | −0.70                 | 0.50                  | 1.50                  |
| SFA-7 | −5.54 | −3.44 | 2.10      | 5.54 | 3.44  | 0.95   | 1.05                  | −0.76                 | 0.34                  | 1.34                  |
| SFA-8 | −5.65 | −3.47 | 2.18      | 5.65 | 3.47  | 0.91   | 1.09                  | −0.73                 | 0.45                  | 1.45                  |

Table 3. Quantum chemical parameters of the SFA-5–8 synthesized sensitizers.
useful parameters that could reflect the system's reactivity. On one hand, hardness could assess the maximal electromotive force between donors and electron acceptors within the same molecule. In this regard, accurate determination of energy gaps can be used to classify a substance as either hard or soft. For instance, a high HOMO–LUMO gap means a hard species, whereas a low HOMO–LUMO gap indicates a soft moiety. Importantly, the global hardness of a pure substance was linked to its stability and reactivity. The reactivity is inversely linked to global hardness, while the stability is closely linked to it. Further insights, the global hardness for SFA-5–8 sensitizers was reported to be $\eta = 1.13 > 1.10 > 1.05 > 1.09$ eV, respectively. The lower hardness ($\eta$) value could be appropriate for allowing an effective charge transfer within the dye molecules. Thereby, SFA-7 could show efficient charge transfer features when compared to its corresponding sensitizers (SFA-5–8). Further, the key photovoltaic parameters such as $\Delta G_{\text{inj}}$, $\Delta G_{\text{reg}}$, and $\Delta G_{\text{rec}}$ were estimated as shown in Eqs. (5–9) and their related data were summarized in Table 3.

$$\Delta G_{\text{inj}}(eV) = E^\text{dye}_\text{OX}^\ast - E_{\text{CB}}$$  
$$\Delta G_{\text{reg}}(eV) = E^\text{dye}_\text{OX} - E_{\text{redox}}$$  
$$\Delta G_{\text{rec}}(eV) = E^\text{dye}_\text{OX}^* - E_{\text{CB}}$$

$\Delta G_{\text{inj}}$ for SFA-5–8 molecules was calculated by $E^\text{dye}_\text{OX}^*$ and $E_{\text{HOMO}}$, and it was found to be $-0.51, -0.70, -0.76,$ and $-0.73$ eV, respectively. This could forecast an adequate driving force for the excited organic molecules to inject electrons into the conduction band (CB) of the TiO$_2$ molecule. That in turn could enhance the $J_{sc}$ values and promote the DSSC efficiency. It could be observed that all driving force values ($\Delta G_{\text{inj}}$) of the synthesized SFA-5–8 dyes are negative, which is ideal for hole injection. Most importantly, SFA-7 had a greater value than the other TPA dyes, confirming that adding one additional acceptor and anchoring moieties (COOH, CN, CO, NH) to the dye molecule could facilitate the charge transfer features, thus better DSSC performance.

For comparison, the predictable dye regeneration values are listed in Table 3 in an ascending order as fellow: SFA-5 (0.76 eV) > SFA-6 (0.50 eV) > SFA-8 (0.45 eV) > SFA-7 (0.34 eV). As reported in Table 3, SFA-7 has the smallest $\Delta G_{\text{reg}}$ value of $\sim 0.10$ eV, demonstrating the maximum dye regeneration capability. Those who reported $\Delta G_{\text{rec}}$ values have been decreased as the following SFA-7 (1.34 eV) < SFA-8 (1.45 eV) < SFA-6 (1.50 eV) < SFA-5 (1.76 eV). When SFA-6–8 sensitizers were injected, three fractions carrying the 2-cyanoacrylamide derivatives with different acceptors had been proposed which could defeat the charge recombination to a specific limit. In this context, SFA-7 has reported the lowest charge recombination value ($\Delta G_{\text{rec}}$) of about 1.34 eV in comparison with other structures in the same class. Accordingly, based on the calculated outcomes of the aforementioned factors $\Delta G_{\text{inj}}$, $\Delta G_{\text{reg}}$, and $\Delta G_{\text{rec}}$, SFA-7 could confirm its superiority as a high efficient dye for DSSCs applications. Moreover, those previous findings could suggest that phenyl acetonitrile and 2-cyanoacetamide of SFA-5–8 compounds might be also viable dyes as good choices for DSSC.

**Electrochemical properties.** Cyclic voltammetry (CV) experiments were conducted to determine the electron transfer feasibility from the SFA-5–8 sensitizers to the TiO$_2$ molecule, as well as to investigate the electron regeneration of the dyes via calculating the ground and excited oxidation potentials of the newly synthesized sensitizers (SFA-5–8). These values represent the key criterion to evaluate the suitability of an organic dye for DSSC applications and provide a deeper insight into the thermodynamic driving force of electron injection and dye regeneration. Such corresponding values are depicted in Fig. 7, GSOP and ESOP were calculated as stated in Eq. (10), where the oxidation onset stands for the onset oxidation potential of CV oxidation peak. GSOP values for the studied SFA-5–8 dyes were found to be: SFA-5 (−5.94 eV), SFA-6 (−5.78 eV), SFA-7 (−5.58 eV), and SFA-8 (−5.68 eV). The HOMO of sensitizers is more negative than the value of $\left(\frac{1}{2}I^\text{e}^\ast/1^\text{e}_0\right)$ (−5.2 eV) reox electrolyte energy level, respectively, thus confirming the possibility of the dye regeneration.

$$\text{ESOP} = \left[\text{GSOP}(eV) + 4.7\right] - E_{0_{\text{red}}} \text{ eV}$$

Additionally, ESOP of sensitizers (SFA-5–8) was estimated from the above-mentioned equation using both the GSOP and $E_{0_{\text{red}}}$ (calculated from the absorption spectra of the sensitizer). The ESOP energy levels are lying between $-3.48$ and $-3.65$ eV for the sensitizers: SFA-5 (−3.65 eV), SFA-6 (−3.55 eV), SFA-7 (−3.41 eV), and SFA-8 (−3.48 eV), respectively. Those values are higher than that of the TiO$_2$ conduction band. It is worth mentioning that the LUMO level of the di-anchoring dyes completely changed for the mono-anchoring counterparts, associated with the conjugation length and the electron-withdrawing character of the synthesized dyes acceptors as well as the HOMO–LUMO minimized band gaps. As expected SFA-6–8 molecules with nitroacanoaceta-mide, carboxycyanoacetamide, and pyridinyl cyanoacetamide as strong acceptor moieties showed the smallest bandgap values compared to that of SFA-5 with the phenylacetonitrile segment. That could be a direct evidence on the highest degree of conjugation between the electron-accepting (CO, CN, NO$_2$, COOH, pyridyl ring) units and donor parts. As could be noticed, all ESOP data are energetically less positive than that of the TiO$_2$ CB.
potential (−4.2 eV), unraveling the efficient injection of the electron to the TiO$_2$ edge. Amongst all synthesized dyes containing cyanoacetamide segments, SFA-7 contains the strongest electron-withdrawing group (COOH) than pyridyl cyanoacetamide of SFA-8 and 4-nitrocyanoacetamide in SFA-6. That in turn could imply a deficient driving force for the electron transfer by possessing the smallest $E_{0-0}$ values and ensuring efficient light capture. All the sensitizers (SFA-5–8) could meet the thermodynamics prerequisite, hence rendering them suitable to be used as effective sensitizers for TiO$_2$-based DSSCs.

**Molecular modeling.** DFT calculations were performed on SFA-5–8 sensitizers using the B3LYP hybrid method in parallel with the d-polarized 6–311G basis implemented in the Gaussian09 program. Figure 8 gives more insights into the relationship between geometric structure and electronic distribution of the HOMOs and LUMOs levels for the four sensitizer dyes. Intramolecular charge transfer (ICT) from the dye HOMO level...
Molecular electrostatic potential (MEP). Molecular electrostatic potentials (MEP) is one of the efficient approaches to identify the internal charge transfer (ICT) property of the entire organic molecules between HOMO–LUMO levels of triphenylamine of SFA-5–8 dyes, which can be obtained from the cube file of the Gaussian job. The effect of donor–acceptor groups was analyzed by inspecting the different HOMO–LUMO levels and (MEPS) of all SFA-5–8 sensitizers (Fig. 9). On one hand, the negative (red) low potentials of SFA-5 are found prominently around the region of the anchoring group which is concentrated on carbonyl, cyano (CN), and NO₂ groups. On the other hand, the negative charge of SFA-6 molecules with cyanoacetamide moieties were localized over cyano, carbonyl, and nitro groups. As for the SFA-7 dye, its negative charge was localized on the cyano group, and carbonyl attached to the COOH group. Furthermore, the negative charge of SFA-8 is founded to be linked to CN, CO, as well as the nitrogen of the pyridine ring. From further insights, the blue positive region of the MEP map was localized over the donor moieties such as the triphenylamine ring, π-conjugation system, and thiophene ring regions, thus demonstrating their favorite sites for nucleophilic attack. Indeed, analyzing all previous MEP features of all synthesized SFA-5–8 sensitizers revealed the electron feasibility for possible interaction with another group of atoms. These findings can reasonably give an indication of the ICT nature of all synthesized SFA-5–8 sensitizers when they are adsorbed on the TiO₂ surface.

**TiO₂ electrode preparation and device fabrication.** TiO₂ fabrication process was thoroughly provided in the “Supplementary information file (SI)”.

Figure 9. Molecular electronic potential diagram (MEP) of SFA-5–8 sensitizers.
Predictably, cells sensitized by N719 shops depicted in Fig. 11. As could be inferred, the enhanced $J_{sc}$ sensitivity was translated into the highest density–voltage spectra for N719, phenylacetonitrile (SFA-5) Jsc values of N719 (17.00 mA/cm²), SFA-8 (16.78 mA/cm²), SFA-6 (16.10 mA/cm²), and SFA-5 (15.16 mA/cm²) counterparts. Such short circuit current enhancement of SFA-7 molecule could be mainly linked to better absorption spectra on the TiO₂ surface.

Photovoltaic device characterizations. To further evaluate the Photovoltaic enhancement and assess the electron injection efficiency of all sensitized devices (SFA-5–8) side by side with the charge carrier efficiency of the adsorbed dyes on the TiO₂ surface, the incident photon-to-electron conversion efficiency (IPCE) was extensively measured under no external bias, as depicted in Fig. 10. That in turn could be a very vital tool for establishing the structure–property relationship, determining the best electron anchoring group for TPA-sensitizers systems, and more importantly, linking the adsorber structure with their corresponding solar performance⁴⁷. As shown in Fig. 10, IPCE values of all DSSC based on SFA-5–8 sensitizers showed maximum IPCE peaks reaching (58–68%) at a range of 300–800 nm, confirming the vital role of phenylacetonitrile and 2-cyanoacetamide derivatives present in all synthesized dyes on enhancing the photoelectrochemical performance. Specifically, SFA-7 reported the highest IPCE peak of above 68% at ~300–800 nm along with the enhanced $J_{sc}$ value amongst all studied dyes. This can be explained based on the fact that incorporating a strong electron-withdrawing carboxylic group (COOH) of the 4-carboxylicamidoacetic acid segment to other anchoring CO and CN moieties of SFA-7 contributed largely to maintaining the highest IPCE value. That was even higher than those reported for N719 dye, thus revealing higher photocatalytic efficiency of 4%. As for the SFA-8 sensitizer, carboxyl group replacement with a pyridyl ring has minimized its electron light-harvesting ability and hindered its electron injection, thus reporting a lower efficiency in contrast to the SFA-7 analogue. Although 4-nitrocyanoacetic acid SFA-6 has the same skeleton of carboxyl and pyridyl 2-cyanoacetamide sensitizers as SFA-7–8 analogs, the IPCE peak of the SFA-6 was found to be lower than its corresponding SFA-7 and SFA-8 sensitizers, mainly highlighting the strength of the electron-withdrawing groups⁴⁸. This lower efficiency could be attributed to the presence of nitro group (NO₂) that strongly promoted the dye aggregation and hindered the IPCE values, as confirmed in Fig. 10. Predictably, cells sensitized by SFA-5 offered weaker absorption with a less covered surface on the TiO₂ surface compared to other SFA-6–8 sensitizers, thus influencing the overall yield and retard the electron injection processes⁴⁹. The $J_{sc}$ IPCE values integrated from the IPCE spectra are in good consistency with the $J_{sc}$ values measured in the J–V measurements. Consequently, the cell with dye SFA-7 gives the highest and broadest IPCE spectrum, confirming its highest $J_{sc}$. The improved IPCE responses are consistent with the improved $J_{sc}$ ⁴⁹. Furthermore, the IPCE spectra of all SFA-5–8 sensitizers and N719 are in good agreement with their UV-vis absorption spectra on the TiO₂ surface.

Table 4 summarizes all corresponding photovoltaic parameters including; short-circuit photocurrent density ($J_{sc}$), open-circuit photovoltage ($V_{oc}$), fill factor (FF), and power conversion efficiency ($\eta_{cell}$). The photocurrent density–voltage spectra for N719, phenylacetonitrile (SFA-5), and 2-cyanoacetamide sensitizers (SFA-6–8) are depicted in Fig. 11. As could be inferred, the enhanced IPCE response of 4-carboxylicamidoacetamide SFA-7 sensitized device was translated into the highest $J_{sc}$ of approximately (17.51 mA/cm²) in comparison with the reported $J_{sc}$ values of N719 (17.00 mA/cm²), SFA-8 (16.78 mA/cm²), SFA-6 (16.10 mA/cm²), and SFA-5 (15.16 mA/cm²) counterparts. Such short circuit current enhancement of SFA-7 molecule could be mainly linked to better absorption.

![Figure 10. Incident-photon-to-current conversion efficiency (IPCE) spectra for all studied SFA-5–8 sensitizers.](image-url)

| Sensitizer (0.2 mM) | $V_{oc}$ (V) | $J_{sc}$ (mA cm⁻²) | $J_{sc}$ IPCE (mA cm⁻²) | FF | $\eta_{cell}$ (%) |
|-------------------|-------------|-------------------|------------------|----|-----------------|
| N719              | 0.67 ± 0.03 (0.70) | 16.96 ± 0.04 (17.00) | 16.95 | 0.59 ± 0.01 (0.61) | 7.21 ± 0.02 (7.25) |
| SFA-5             | 0.62 ± 0.01 (0.63) | 15.14 ± 0.02 (15.16) | 13.99 | 0.67 ± 0.02 (0.69) | 5.51 ± 0.03 (5.53) |
| SFA-6             | 0.62 ± 0.03 (0.64) | 16.05 ± 0.06 (16.10) | 15.86 | 0.54 ± 0.01 (0.56) | 5.69 ± 0.13 (5.77) |
| SFA-7             | 0.71 ± 0.02 (0.72) | 17.49 ± 0.01 (17.51) | 16.95 | 0.58 ± 0.03 (0.60) | 7.32 ± 0.25 (7.56) |
| SFA-8             | 0.63 ± 0.03 (0.65) | 16.77 ± 0.02 (16.78) | 16.27 | 0.56 ± 0.04 (0.59) | 6.36 ± 0.13 (6.43) |
employed for the adsorption of carboxylates. The presence of a second strong anchoring group (COOH) as an electron acceptor, given excellent electron-withdrawing capabilities relative to the Brønsted acid sites, can be crucial for enhancing the electron injection efficiency to TiO2 conduction band compared to other sensitizers. That was also confirmed by the highest value of its LUMO levels. In a bid to further examine the photovoltaic performance of the synthesized sensitizers, open-circuit voltage and fill factor could give insights into the photoelectrochemical performance of the synthesized sensitizers. For instance, N719 and SFA-5–8 dyes yielded power conversion efficiency (% ηcell) of 7.25 (Voc = 0.70 V and FF = 0.61), 5.53 (Voc = 0.63 V and FF = 0.69), 5.77 (Voc = 0.64 V and FF = 0.56), 7.56 (Voc = 0.72 V and FF = 0.60), and 6.43 (Voc = 0.65 V and FF = 0.59), respectively. The Voc of sensitizers follows the order of SFA-7 > N719 > SFA-8 > SFA-6 > SFA-5.

As stated in Table 4, SFA-5, the anchoring occurs through the cyano group (CN) working as a withdrawing group, and the coordination between the nitro group and the TiO2 surface causes optical bleaching of the light absorption, increases the dye/TiO2 coupling, which provides the process of anchoring on the surface TiO2. Nitrophenyl acetonitrile sensitizers (SFA-5) showed the lowest efficiency attributed to the weakest acceptor moieties compared to other 2-cyanoacetamides sensitizers (SFA-6–8) and showed the lowest values of Jsc and Voc values. For SFA-6, by replacing the phenyl acetonitrile by 4-nitrocyanoacetamide, the anchoring process occurs through a carbonyl group (CO), (NH), (NO2), and (CN) groups that work as excellent withdrawing groups which provide the process of anchoring on the surface TiO2, increasing the number of anchoring function groups enhanced the efficiency than anchoring by only (CN) and (NO2) in SFA-5, the highest Jsc and better Voc values were reported for the 4-carboxylycyanocetamide SFA-7 sensitizer associated with a higher photoconversion efficiency of about 7.56%, thus outperforming the best-reported dyes which mainly related to the various strong acceptor’s group, carbonyl group plays a great role in surface adsorption on TiO2 addition to act as electron acceptor, given excellent electron-withdrawing capabilities relative to the Bronsted acid sites employed for the adsorption of carboxylates. The presence of a second strong anchoring group (COOH) as an extra acceptor addition to the various anchors across the 2-cyanoacetamide segment (CO), (CN), and (NH) act as bifunctionality of acceptor and electron-withdrawing groups which seems to enhance the performance of the sensitized cells and the electron injection into the conduction band of TiO2 through H-aggregates. This is not surprising as the photoconversion efficiency of the SFA-7 sensitizer was raised by 4% with respect to N719. Finally, for SFA-8, using 4-pyridilycyanocetamide for the first time as a new bifunctionality anchoring and electron withdrawing system, by the formation of coordination bonds between the nitrogen atom in the pyridyl ring of the Lewis acidic sites of the TiO2 surface leads to efficient electron injection, addition to the electron-withdrawing groups across the 2-cyanoacetamide segment (CO, NH and CN groups). Moreover, SFA-6 and SFA-8 sensitizers carrying 2-cyanoacetamide segments showed lower efficiency than SFA-7, which mainly related to the strength of the anchoring group in the order of COOH > pyridyl > NO2. Thus, Jsc and Voc values have been changed accordingly. Based on the above findings, it could be noticed that the experimental results are in accordance with the theoretical predictions.

Electrochemical impedance spectroscopy (EIS). To better correlate the charge dynamic characteristics of all synthesized SFA-5–8 sensitizers with the enhanced photocatalytic performance, electrochemical impedance spectroscopy (EIS) was investigated to effectively determine the charge transfer resistance (Rct) and the interfacial capacitance at the TiO2 electrode/dye/electrolyte and Pt/electrolyte interfaces. Figure 12 shows the Nyquist plots of all sensitized cells based on phenylacetonitrile, 2-cyanoacetamide SFA-5–8 and N719 sensitizers. As depicted in Fig. 12, EIS data showed two distinct semicircles that were properly fitted using simplified Randles equivalent circuit. A small semicircle observed in the low-frequency region could represent the cathode charge transfer resistance which is directly related to FF. On the other hand, a large semicircle was observed in the middle frequency regime that could be originated from charge transfer resistance (Rct) from TiO2 molecule to the electrolyte solution, which is directly related to the Voc. According to Nyquist plots, the semicircle radius of all sensitized SFA-5–8 cells follow the order of SFA-7 > N719 > SFA-8 > SFA-6 > SFA-5. It is worth noting that the Voc of 4-carboxylycyanocetamide SFA-7 is larger than that of the N719 counterpart, indicating that the charge...
carriers recombination process was retarded upon sensitization. In addition, the high $R_{rec}$ value of the SFA-7 molecule upon sensitization could be mainly ascribed to the SFA-7 structure containing various acceptors and anchoring moieties that are favorable for retarding charge recombination process. To this end, Nyquist plots unravel that sensitization by 2-cyanoacetamide sensitizers could be beneficial for reducing dark current and suppressing charge recombination at the TiO$_2$/dye/electrolyte interface\textsuperscript{52}.

On the other hand, EIS could be represented using Bode frequency plots, as illustrated in Fig. 13. That was estimated using the following equation; ($\tau_{ef} = 1/2\pi f$)\textsuperscript{52}, where $t$ represents the electron lifetime injected into TiO$_2$ and $f$ is the mid-frequency peak in bode plots, which is directly related to the electron lifetimes. Notably, the electron lifetime that is mainly related to $V_{oc}$ was determined for all synthesized SFA-5–8 molecules using Bode frequency plots. The values of the mid-frequency peaks of the bode plots followed the order of SFA-7 > N719 > SFA-8 > SFA-6 > SFA-5, corresponding to electron lifetimes in the sequence of SFA-5 < SFA-6 < SFA-8 < SFA-7. Similarly, the corresponding electron lifetimes were found to be 4.48, 3.25, 2.58, 2.14, and 1.26 ms, respectively, in agreement with $V_{oc}$ values. For the sensitized SFA-5–8 and N719 dyes, the electron lifetimes follow the order of SFA-7 > N719 > SFA-8 > SFA-6 > SFA-5, respectively, which lead to a significant enhancement in photocurrent and photovoltage and considerably higher cell efficiency\textsuperscript{53}.

**Conclusion**

In summary, we have synthesized four innovative phenylacetonitrile and 2-cyanoacetamide derivatives of dyes SFA-5–8 with different auxiliary donors and acceptors. We studied how the presence of a thiophene spacer and different auxiliary acceptors (NO, CO, CN, COOH, and pyridyl groups) affected the photophysical and electrochemical performance of DSSC devices. DFT and TD-DFT were used to explore the photophysical and electronic structures of all studied SFA-5–8 organic dyes. The molecular orbital energy levels of SFA-5 sensitizers possessed an appropriate thermodynamic driving force that was sufficiently suitable for electron injection from the LUMOs into the TiO$_2$ conduction band. The calculated studies of the dihedral angle and NBO of SFA-5–8 revealed an efficient ICT across sensitizers from the donor to acceptor parts. The higher electron acceptance and lower chemical hardness values of SFA-5–8 molecules suggested excellent photoelectric conversion performance.
Further, we measured the photovoltaic properties to properly investigate the direct effect of various anchoring units on the overall performance of the DSSCs. The overall photocurrent conversion efficiency of DSSCs for all SFA-5–8 sensitizers was approximately 5.53–7.56%. The number of sensitizers loaded into the TiO₂ surface is in accord with the Jsc values. Remarkably, SFA-7 showed superior photocurrent conversion efficiency associated with the highest Jsc and Voc which could be attributed to reduced recombination rates of charge carriers and the increased electron lifetime. The sensitizations of the new SFA-5–8 sensitizers were investigated in comparison to the N719 dye. Interestingly, the optimized SFA-7 attained a higher PCE by approximately 4% over that of N719 sensitized one. This splendid activity can be ascribed to the excess anchoring groups of the synthesized dyes that could lead to a longer blocking layer that minimizes charge recombination. Such breakup of π-stacked aggregates could improve the electron injection yield, rendering SFA-5–8 sensitizers superior candidates for applied DSSC applications.

Data availability

The datasets used and/or analyzed during the current study available from the corresponding author on reasonable request.

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**Author contributions**

S.A.B.: synthesis, methodology, and graphical plots. E.A.-L. and A.A.F.: supervision, initial corrections, and comments. M.R.E.: synthesis, writing original draft, data analysis, editing, proofreading, and manuscript handling. All the authors read and approved the final manuscript.

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**Additional information**

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