A Triphenylamine Substituted Quinacridone Derivative for Solution Processed Organic Light Emitting Diodes

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ABSTRACT:

We report on a novel quinacridone derivative design, namely, 2,9-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-5,12-bis(2-ethylhexyl)-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-dione (**TPA-QA-TPA**) for possible use as a solution processable emissive layer in organic light emitting diodes (OLEDs). **TPA-QA-TPA** contains branched alkyl chains for enhanced solubility and methoxytriphenylamine moieties (TPA) as end capping groups. The

end capping groups not only extend the molecular conjugation leading to a red shifted emission, but have a propeller shaped conformation. The propeller design hinders the intermolecular π - π stacking, hindering aggregation and hence suppressing concentration quenching of the fluorophores in the solid state. The new molecular design shows good thermal stability, with a decomposition temperature of 390 °C and a melting temperature of 295 °C. The absorption and emission maxima for **TPA-QA-TPA** compound are 552 and 622 nm respectively. Using **TPA-QA-TPA** as a dopant in tris(8-hydroxyquinolino)aluminum (Alq₃), organic light emitting diodes were realized in a simple device structure.

Highlights:

- ❖ Quinacridone and triphenylamine based molecule TPA-QA-TPA was synthesized & characterized.
- ❖ The end capping groups provide propeller shaped conformation with orange red emission.
- ❖ The propeller design hinders the intermolecular π - π stacking & aggregation in thin film.
- ❖ TPA-QA-TPA was successfully used as an emissive layer in the organic light emitting diodes.

KEYWORDS: Quinacridone, Triphenylamine, Solution process, Fluorescence, Organic Light Emitting Diode.

1. Introduction

Quinacridone (QA) based molecules are commonly used as organic pigments and their numerous derivatives have been also successfully used in industrial colorant applications such as inkjet toners and robust outdoor paints [1-3]. QA is a low cost material and proved to be an outstanding core building block for designing and synthesizing new aromatic functional materials. Due to its planar fused molecular structure, ability to support π - π stacking, intense

fluorescence, high charge carrier mobility and intermolecular H-bonding, QA and its derivatives can be used as potential organic semiconductors in various organic electronics devices. QA based functional organic semiconductors have been successfully used in various devices including organic light emitting diodes (OLEDs) [4], organic thin film transistors (OTFTs) [5] and organic photovoltaics (OPVs) [6,7]. Among these applications, particularly OLED devices have recently attracted further attention to this class of molecules due their properties such as intense green/yellow electroluminescent emission, strong absorption in the visible-light region, good carrier properties and good thermal and electrochemical stability [4,8-10]. The popularity of OLEDs has experienced a growth due to their application in high-performance commercial displays owing to the several advantageous characteristics, including clear bright colours, large area processing, high energy efficiency and possibility of realizing flexible displays [11,12]. Furthermore, OLEDs have also expanded their applications into solid state lighting solutions [13,14].

Research into efficient, easily synthesized and stable materials for solution processed light emitting molecules has been a highly demanding and challenging area in the development of increasingly efficient and highly luminescent OLED devices [15,16]. The design of red/orange emissive molecules for the OLED industry is particularly challenging as most red emissive molecules are less flexible considering in the scope of their use when compared to blue/green emitting complexes. This inflexibility is rooted to the nature of red emissive molecules, due to their polar and/or extensively π conjugated form, which in turn leads to strong tendency to aggregate due to dipole-dipole or π stacking intermolecular forces. The molecular aggregation is highly undesirable as it results in strong quenching leading to great emission intensity decrease [17,18].

Small-molecule conjugated materials have been identified as a possible alternative for OLED emissive layers due to their facile synthesis in combination with low-cost solution

deposition processes [19]. Furthermore, the high cost, often poor efficiency and poor chemical stability of metal based complexes for the application in OLEDs encourage the development of fully organic light emitting molecules [17]. Considering the quinacridone pigment, the possibility of red-shifting the QA emission through molecular manipulation and design is also attractive due to the importance of the red light component in OLED devices.

Even though QA derivatives carry promising characteristics for emissive layers in OLED devices such as exceptional thermal stability as well as simply modified chemistry [1], their use in such systems is seldom reported. A recent work by C. Wang et. al. shows the successful extension of the QA backbone by the addition of **diphenylamine** moieties as end-capping groups to the primary QA molecule [8]. The synthetic addition elongates the conjugation of the molecule resulting in a red-shifted emission and improved thermal properties. Furthermore, in the attempt at reducing aggregation of QA derivatives, another work by C. Wang has also documented the addition of pentaphenylphenyl moieties to the quinacridone backbone, creating a propeller-shaped conformation which hinders the intermolecular π - π stacking, successfully suppressing aggregation of the fluorophores in the solid state [20].

Taking inspiration from previous works, our investigation realizes the synthesis of a quinacridone derivative with end capping methoxytriphenylamine moieties (TPA), namely, 2,9-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-5,12-bis(2-ethylhexyl)-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-dione (**TPA-QA-TPA**). The introduction of TPA end capping units allows for the further extension of the conjugated backbone when compared to the **diphenylamine** quinacridone, possibly further enhancing the charge carrier mobility of the compound. It has been well documented that the TPA substituted conjugated derivatives have proven to be best class charge transport materials for various devices. In addition, the TPA unit was believed to behave in a similar way to the propeller shaped pentaphenylphenyl

moiety described in the previous work by Wang [20] which shows the capability to hinder the undesired molecular aggregation which quenches the final emission of the quinacridone derivative. In addition, we have also introduced two branched alkyl chains (ethylhexyl) to the core quinacridone, further adding to the molecular design by enhancing solubility of the small molecule. Lastly, OLEDs using **TPA-QA-TPA** were realized using a simple device structure ITO/PEDOT:PSS/Alq₃:**TPA-QA-TPA** (3 wt%)/LiF/Al.

2. Results and Discussion

2.1. Synthesis of TPA-QA-TPA

Firstly, the commercial available cheap quinacridone dye was alkylated at heating to reflux condition using ethyl hexyl bromide in presence of phase transfer catalyst tetrabutylammonium bromide (TBABr), strong base sodium hydroxide (NaOH) in toluene. The ethyl hexyl substituted quinacridone derivative was then brominated using harsh bromination reaction conditions using molecular bromine and acetic acid for 1 h at 110 °C. The final dibromo alkyl substituted quinacridone was then purified by recrystallization in ethyl acetate yielding red crystals. The dibrominated ethyl hexyl substituted quinacridone derivative 2,9-dibromo-*N,N'*-di(2-ethylhexyl)quinacridone acts as a starting precursor (Fig. S1) for designing various functional organic semiconductors [21]. Another precursor 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (Fig. S1) was produced from its brominated derivative using butyl-lithium in a per-literature procedure [22]. The target **TPA-QA-TPA** compound was synthesized by classical Suzuki coupling reaction between the dibrominated ethyl hexyl substituted quinacridone derivative 2,9-dibromo-*N,N'*-di(2-ethylhexyl)quinacridone and the monoboronic ester of methoxy-substituted triphenylamine 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline as demonstrated in the Scheme 1. The documented reaction

is of great interest as starting from an inexpensive quinacridone dye molecule, a high end complex molecule is synthesized in an uncomplicated manner, without the requirement for extreme conditions or extensive reaction times. The yield of the Suzuki coupling reaction was found to be of 61% (Fig. S3). The **TPA-QA-TPA** is a donor-acceptor-donor (D-A-D) compound where the end capping triphenyl amine group acts a donor whereas the central quinacridone acts as an acceptor moiety.

Scheme 1: Synthesis route of precursor building blocks and **TPA-QA-TPA**

2.2. Thermal Properties

The thermal properties of the newly synthesized compound **TPA-QA-TPA** were studied through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques (Fig. 1). The 5% weight loss of **TPA-QA-TPA** was observed at 390°C and the reported decomposition temperature (T_d) is very high. Such a high thermal stability is extremely good for fabricating organic electronic devices using various annealing conditions. The DSC analysis of **TPA-QA-TPA** revealed a melting temperature (T_m) of 295°C and main

crystallization temperature (T_c) of 230 °C. Additionally, during the heating scan, a cold crystallization peak appeared at 188 °C because the compound might undergo some small amount of crystallization while heating. During the cooling cycle, apart from the major crystallization transition, there is a another minor enthalpy transition at 204 °C, which is attributed to the rotation or minor structural reordering of the alkyl chains [23]. When compared to the straight Octyl (C_8) chain substituted diphenylamine attached quinacridone derivative (C8-QA) presented by Wang [8], (T_m = 179 °C, T_d = 370 °C), the thermal stability of our branched ethyl hexyl substituted with triphenyl end capping group **TPA-QA-TPA** compound shows an obvious improvement and this is arising due to the molecular weight provided by extra phenylene group at the both side of QA moiety. The sharp melting point clearly exhibits the weak degree of crystalline behavior of **TPA-QA-TPA** compound arising from the fused QA core and intramolecular H-bonding between carbonyl group and hydrogen substituted on adjacent phenylene moiety.

Fig.1: (a) TGA thermogram and (b) DSC curve of **TPA-QA-TPA** with a scanning rate of 10 °C/min.

2.3. Theoretical Calculations

In order to gain a deeper insight into the molecular geometry and electronic structure, Density Functional Theory (DFT) [24,25] calculations were performed at the B3LYP [26] level of theory using the basis set 6-31g+(d,p). A polarized continuum model of the DCM (for comparison with CV data) as well as chloroform (CF) and toluene (Tol) (for comparison with optical property measurements) solvents was used [27]. The calculations were performed in Gaussian 09 [28]. Optical absorption and emission spectra were computed with Time-Dependent (DFT) [29]. The emission spectrum was computed by optimizing the lowest excited state. As shown in Fig. 2, the highest occupied molecular orbital (HOMO) of **TPA-QA-TPA** is delocalized along the entire backbone, whereas the lowest unoccupied molecular orbital (LUMO) of the compound is much more localized around the central electron accepting quinacridone unit. The computational results show that the HOMO and LUMO energy levels of **TPA-QA-TPA** were -4.99 and -2.66 eV, respectively. Comparing the theoretical results for the synthesized **TPA-QA-TPA** molecule presented in this work with the simple C8 alkyl chain quinacridone molecule with diphenylamine substituted end capping group reported by C.Wang [8], we could recognize that the addition of the end capping triphenyl amine units to the quinacridone backbone can be seen to affect the conjugation length due to extra phenylene unit. **TPA-QA-TPA** exhibits a theoretical HOMO-LUMO gap of 2.33 eV whereas diphenylamine substituted C8-QA molecule shows the theoretical HOMO-LUMO gap of 2.74 eV. As a consequence of enhancement in conjugation due to extra phenylene unit (diphenylamine vs triphenylamine end capping groups) reduces the HOMO-LUMO gap. Such observations are well supported in terms of physical red color appearance and a red shift in the emission spectrum under a UV lamp.

The computed absorption and emission spectra are shown in Supporting Information (Fig. S4). The computed absorption peaks around 600 nm in both CF and Tol are in good

agreement the measured peaks (Fig. 3a). The computed absorption peak in CF (604 nm) is only slightly red-shifted vs. that in Tol (592 nm), in agreement with the experiment. The computed absorption and emission peaks are red-shifted vs. experiment by about 0.2 eV, as expected with B3LYP [30].

Fig. 2: Molecular modelling geometry and calculated HOMO/LUMO values of **TPA-QA-TPA**.

2.4. Photophysical Properties

The optical properties of newly synthesized molecule and precursor were characterized using UV-vis and photoluminescence spectroscopy. In order to study the effect of triphenyl amine end capping groups on the quinacridone core, we characterized starting alkyl substituted dibromo precursor (C8-QA-Br compound 3 in the Scheme). The C8-QA-Br shows absorption and emission maxima at 530 and 549 nm respectively (Fig. S4); whereas our newly synthesized **TPA-QA-TPA** molecule exhibits longer absorption and emission

maxima with values of 552 and 622 nm respectively. Almost a 70 nm difference between absorption and emission spectrum represents the Stokes shift and such a large stoke shift is expected for the rigid molecular structure. The higher Stokes shift of **TPA-QA-TPA** also suggests that the excited state structural geometry of TPA-QA-TPA molecule is different to its ground state geometry. Just as observed in both works by Wang, the more extensively conjugated synthesized molecules present a bathochromic shift when compared to the quinacridone moiety [8,20]. Similarly, for **TPA-QA-TPA** molecule, the bathochromic shift was found to be 22 and 73 nm for the maxima of λ_{abs} and λ_{em} when compared to the simple quinacridone moiety. Table 1 summarizes the electrochemical and photophysical results for **TPA-QA-TPA** molecule.

Furthermore, the absorption and emission spectra of Alq₃ was also investigated since Alq₃ was used as a host material together with **TPA-QA-TPA** guest molecules in the emissive layer of the OLED device. Such guest-host systems can show emission through energy transfer from the host material to the fluorescent dopant through Dexter and Forster energy transfers [31,32]. Enhanced functioning of the guest/host emissive layer is present when energy transfer between the host and guest materials is optimized. Optimizing the energy transfer requires tuning of the overlap of the host's emission spectrum and the dopant absorption spectrum; a suitable overlap results in enhanced energy transfer [31].

Optical properties of **TPA-QA-TPA** and Alq₃ are demonstrated in Fig. 3, in which absorption and emission data of thin film and solution is present as well as photoluminescence quantum yield (PLQY) values. Fig. 3(a) shows the absorption and emission spectra of **TPA-QA-TPA** in two solvents, CF and Tol. The spectral shift in the **TPA-QA-TPA** emission spectra is due to solvatochromism because of increase of solvent polarity from Tol to CF. Similar solvatochromism behavior has also been reported by Wang in his work with a quinacridone derivative [8,20]. The interaction between the solvent and

excited states of the chromophore are the origin for the solvent dependent effect; in the case for **TPA-QA-TPA**, an increased solvent polarity leads to a bathochromic shift of near 100nm when comparing the data for CF and Tol. Furthermore, the solvatochromism also poses as an explanation to the decrease in the photoluminescence quantum yield between **TPA-QA-TPA** in Tol (0.73), and in CF (0.02). As suggested by A. Marini et al [33], solvent-solute effects can affect the nature of the chromophore as well as cause a reduction in the quantum yield.

From the optical data on Alq₃, Fig. 3(b), and **TPA-QA-TPA** spectra of Fig. 3(a) a correlation of Alq₃ emission and **TPA-QA-TPA** absorption can be observed. The maximum emission wavelength of Alq₃ (~520nm) is located within the absorption spectrum of the emissive chromophore **TPA-QA-TPA**; which theoretically indicates a good energy transfer between the host-guest molecules in the emissive layer; confirming the appropriate choice of Alq₃ as the host molecule. Such an energy transfer system with Alq₃ and **TPA-QA-TPA** should result in a device in which **TPA-QA-TPA** would be responsible for the largest system's emission. As a consequence of the energy transfer, a red color emission should be observed instead of pure green, typical of Alq₃.

Furthermore, thin film data on **TPA-QA-TPA** and **TPA-QA-TPA (3%)/Alq₃** systems are demonstrated in Fig. 3(c). The guest-host system shows a slightly blue shifted emission spectrum when compared to the **TPA-QA-TPA** system alone which is likely the result of incomplete energy transfer from host to guest moieties, leading to the presence of some Alq₃ host molecules emission. This can be seen as the shoulder at around 500 nm in the blue spectrum in Fig. 3(c). This blue shift may be due to reabsorption of luminescence from **TPA-QA-TPA** in the neat film of **TPA-QA-TPA**. For **TPA-QA-TPA/Alq₃** film, concentration of **TPA-QA-TPA** is much lower than that for the neat **TPA-QA-TPA** films. Accordingly, reabsorption effect of photoluminescence for blend film becomes pronounced. Another possibility is the difference between film and dopant, namely the red-shift is caused by the

intermolecular interaction between **TPA-QA-TPA** in the neat films. Additionally, an increase in the PLQY is observed for the guest-host system (0.18) when compared to the non-doped **TPA-QA-TPA** (0.06); such a tripling of the PLQY is likely a direct result from the energy transfer between the highly luminescent host Alq₃ and the quinacridone dopant. Demonstrating that the emissive properties of **TPA-QA-TPA** are enhanced by such an energy transfer system.

Fig. 3: Spectrophotometry results. (a) Absorption and emission spectra of **TPA-QA-TPA** in chloroform (CF) and toluene (Tol); (b) Absorption and emission spectra of Alq₃ in Tol; (c) Thin film data of **TPA-QA-TPA** and **TPA-QA-TPA(3%)**/ Alq₃.

2.5. Electrochemical Properties

The electrochemical behavior of the newly synthesized **TPA-QA-TPA** compound was performed by cyclic voltammetry (CV) using a glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum counter electrode respectively. 0.1 M tetra(*n*-

butyl)ammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) dissolved in DCM was used as an electrolyte solution at a potential scan rate of 100 mV/s. The reference electrode (Ag/Ag^+) was calibrated by the standard ferrocene/ferrocenium (Fc/Fc^+) redox couple (4.8 eV below the vacuum level). The electrochemical data of **TPA-QA-TPA** are summarized in Table 1. As shown in Fig. 4, **TPA-QA-TPA** exhibited two reversible and one quasi-reversible oxidation peak in oxidation cycle whereas in a reduction cycle quasi-reversible reduction peak was observed. Due to the presence of electron donating triphenyl amine and extra phenylene unit of quinacridone present in the conjugated backbone responsible for multiple oxidation peaks. Whereas one peak present in reduction cycle is due to the presence of electron withdrawing carbonyl groups of quinacridone. Overall, multiple redox peaks involves coupled electron transfer reactions [34]. The oxidation and reduction onset values were calculated by taking intersection of baseline to the rising current point from the CV data. The HOMO and LUMO values for all materials were calculated using oxidation and reduction onset values using the standard equation $\text{HOMO} = -E_{\text{HOMO}} = e (E_{\text{onset(ox)}} + 4.8) \text{ eV}$ and $-E_{\text{LUMO}} = e (E_{\text{onset(red)}} + 4.8) \text{ eV}$.

Fig. 4: Cyclic voltammograms for the estimation of the HOMO energy level of **TPA-QA-TPA**. The oxidation (a) and reduction (b) were measured in DCM/0.1M Bu_4NPF_6 at a scan rate of 100 mV/s.

Table 1. Optical and electrochemical data for the **TPA-QA-TPA**

Compound	λ_{abs} (nm)		λ_{em} ^a (nm)	E_g^{opt} (eV)	E_g^{cv} ^a (eV)	HOMO (eV)	LUMO (eV)
	Solution	Film					
TPA-QA-TPA	374, 552	378, 551	622	2.12	1.91	-5.00	-3.09

^a Emission maximum in chloroform solution. ^b Electrochemical bandgap = |HOMO - LUMO|

The HOMO and LUMO values of **TPA-QA-TPA** compound was measured -5.0 and -3.09 eV, respectively. In comparison with theoretical calculations, the experimentally estimated HOMO is in excellent agreement while LUMO is off by 0.45 eV. This could be due to the accuracy of approximations, e.g. theoretical calculations have been performed with an idealized model of the solvent whereas the electrochemical analysis has been performed using various electrodes, electrolyte and solvent conditions.

2.6. OLED Device Characteristics

To investigate the electroluminescent properties of **TPA-QA-TPA**, a simple structure of OLED with a configuration of [ITO/ PEDOT:PSS (20 nm)/Alq3: 3 wt% **TPA-QA-TPA** (50 nm)/LiF (1nm)/Al] as shown in inset of Fig. 5(a) was fabricated. A host-guest system of the emissive layer was used with 3 wt% of **TPA-QA-TPA** as dopant in the (tris(8-hydroxyquinoline)aluminium) (Alq₃) host. The emissive layer was sandwiched between ITO/PEDOT: PSS [poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)] on the anode side and LiF (lithium fluoride) /Al on the cathode side. Normalized electroluminescent spectrum of the OLED is shown in Fig. 5(a) and the chromaticity diagram indicating CIE coordinates is shown in Fig. 5(b). Inset of 5(b) shows light emission from the OLED with structure shown in the inset of 5(a). The OLEDs had a turn on voltage ($V_{\text{turn-on}}$) of ~ 6.4 V and reached a maximum luminescence (L_{max}) of ~ 800 cd/m². A maximum current efficiency

($LE_{\max}$) and external quantum efficiency ($EQE_{\max}$) of 0.42 cd/A and 0.2%, respectively, were achieved. Current density and luminance characteristics with respect to voltage, and current efficiency and EQE with respect to luminance are shown in supplementary information (Fig. S7). In comparison to earlier reported **diphenylamine** substituted quinacridone (NPh2-QA) doped Alq₃ based OLED devices,⁸ herein we used PEDOT: PSS (HOMO- 5.1eV) as a hole transporting layer instead of N,N',-di-(naphthalen-1-yl)-N,N'-diphenylbenzidine (NPB HOMO- 5.5 eV). In our device fabrication strategy, we adopted a simple solution processable approach for the deposition of PEDOT:PSS rather than vacuum deposition of NPB hole transporting layer. In order to compare and study the effect of **diphenylamine** vs triphenylamine substituents attached to quinacridone dye core on OLED performance, we compared OLED device parameters and this is listed in Table 2.

Upon comparing the mentioned parameters, a decrease in the device's performance is observed for our **TPA-QA-TPA** and this is might be due to different device geometry, active layer thickness and interlayer interfaces arising due to different set of hole transporting materials used in both cases. Additionally, the energy offset between PEDOT:PSS HOMO value and **TPA-QA-TPA** HOMO value is almost negligible and there might be some losses in transporting holes for the further recombination with injected electrons from cathode. The **TPA-QA-TPA** device showed orange emission with an emission maximum at 600 nm and Commission Internationale de l'Eclairage (CIE) coordinates of (0.56, 0.43) at maximum luminance whereas for NPh2-QA, the emission maximum was observed at 628 nm with CIE coordinates (0.62, 0.36). From our OLED device colour, it is quite clear that the emission of light in the red region is observed, indicating efficient energy transfer from the host Alq₃ to the guest **TPA-QA-TPA**.

Fig. 5: (a) Electroluminescent spectrum of OLED with **TPA-QA-TPA** red dopant in Alq_3 . Inset shows OLED device structure. (b) The emission colour of **TPA-QA-TPA** dopant OLED in CIE coordinates. Inset shows emission from the OLED.

Table 2. Performance of OLED device

Emissive layer	L_{max} (cd/m^2)	LE_{max} (cd/A)	EQE_{max} (%)	$V_{\text{turn-on}}$ (V)
TPA-QA-TPA (3%)/ Alq_3	800	0.42	0.2	6.4
NPh2-QA (3%)/ Alq_3	6239	1.08	1.05	4

3. Experimental Section

3.1. Materials and Instruments

All starting materials were purchased commercially as analytical reagents and used directly without any further purification. Compound 2,9-dibromo-5,12-bis(2-ethylhexyl)-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-dione and 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline

were prepared according to the literatures [21,22]. Synthesized compounds were characterized by ^1H -NMR and ^{13}C -NMR spectrum, which were obtained with a Bruker Ascend 600 spectrometer. Thermal analysis was performed using a Pegasus Q500TGA thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Differential scanning calorimeter (DSC) was conducted under nitrogen using a Chimaera instrument Q100 DSC. The sample was heated at $10\text{ }^\circ\text{C}/\text{min}$ from $30\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$. UV-vis absorption and photoluminescence (PL) spectra of materials were recorded on UV-1800 Shimadzu and Cary Eclipse Fluorescence Spectrophotometer, respectively. Photoluminescence quantum yield (PLQY) measurements were carried out with an Absolute PL Quantum Yield Spectrometer (Hamamatsu, C11347). The cyclic voltammetry (CV) was performed by a Potentiostat Galvanostat with a three electrode cell in a solution of Bu_4NPF_6 (0.1M) in freshly distilled DCM at a scan rate of 100 mV/s . The counter electrode was a Pt wire, the working electrode was glassy carbon and a Ag/Ag^+ electrode was used as the reference electrode.

3.2. OLED fabrication and characterization

Pre-patterned ITO substrates (Kintec) were light scrubbed using a cotton tip in a solution of Alconox in de-ionized water, followed by rinsing several times in de-ionized water. The substrates were then ultra-sonicated in de-ionised water, acetone and isopropanol consecutively for 10 minutes each before blow drying it with compressed air. Using a Laurell Technologies spin coater, PEDOT:PSS (Heraeus) filtered using a $0.45\mu\text{m}$ PVDF filter was spin coated on the ITO substrates at 5000 rpm for 30 seconds. Once the PEDOT:PSS was removed from the contact pads, the substrates were dried on a hot plate at $125\text{ }^\circ\text{C}$ for 20 minutes to remove excess water. Following this, the substrates were transferred to a glove box system with low

moisture and oxygen ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). Solutions of **TPA-QA-TPA** and Alq_3 in anhydrous chloroform, prepared individually with concentration of 10 mg/ml for both, were mixed in the correct ratio to give a solution with 3 wt% **TPA-QA-TPA**. This solution was spin coated on top of the PEDOT:PSS layer to form the emissive layer using a Speciality Coasting Systems spin coater at 1500 rpm for 30 seconds. After removing emissive layer from the contact pads, the films were annealed at 100 °C for 20 minutes to remove residual solvents. LiF/Al electrodes defined using a shadow mask were deposited on top to complete the device structure using a torpedo vacuum thermal evaporator at pressures $\sim 10^{-6}$ mbar. The OLEDs had a pixel area of 10 mm². The devices were encapsulated using customized glass caps and UV curable epoxy (NOA 61, Norland Products) and taken outside the glove box for characterization. A Keysight B2901A sourcemeter interfaced with a Konica Minolta CS-200 luminance meter was used to measure the current-voltage-luminance characteristics of the OLEDs. The electroluminescence spectra of the devices were recorded using a UV-vis spectrometer (USB4000, Ocean Optics). EQE of the devices were calculated using methods for a Lambertian emitter. Thicknesses of the constituent layers of OLEDs were measured using a Bruker Dektak XT profilometers.

3.3. Synthesis

3.3.1. Synthesis of 2,9-dibromo-*N,N'*-di(2-ethylhexyl)quinacridone:

Quinacridone (1) (5.0 g, 16.03 mmol) and tetrabutylammonium bromide (20.6 g, 64.12 mmol) were dissolved in toluene (300 mL) in a one litre round-bottom flask. While stirring, 50% NaOH (20 mL) and 2-ethylhexyl bromide (7.1 g, 36.9 mmol) were added slowly. The reaction mixture was heated to a reflux for 26 h. The reaction mixture was quenched with water (30 mL) and filtered. The organic layer from the filtrate was separated, and the solvent was removed under reduced pressure. The resulting crude product was purified by column

chromatography eluting with dichloromethane (DCM) yielding the product as red solids (2.00 g). This purified red solid and NaOAc (0.793 g, 9.67 mmol) was then mixed and stirred in 75 mL acetic acid and heated to reflux. A solution of bromine (1.37 g, 8.70 mmol) in 5 mL acetic acid was added dropwise and allowed to stir for 1 h at 110 °C. The mixture was cooled to room temperature, and the precipitate was collected and washed with 2% NaOH and water. The crude product was recrystallized in ethyl acetate yielding the product as red crystals (1.80 g, 78%). ¹H NMR (400 MHz, CDCl₃): δ 8.63 (s, 2H), 8.53 (d, *J* = 6.6 Hz, 2H), 7.72 (dd, *J*₁ = 1.2 Hz, *J*₂ = 8.4 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 4.40 (s, 4H), 2.07 (m, 2H), 1.47-1.21 (m, 20H), 0.95 (t, *J* = 4.4 Hz, 6H), 0.85 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (CDCl₃, ppm): δ 177.00, 141.88, 137.36, 136.33, 130.54, 126.18, 122.46, 117.87, 114.93, 114.50, 50.18, 38.67, 31.32, 29.15, 24.73, 23.39, 14.32, 11.54.

3.3.2. Synthesis of 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline:

4-Bromoaniline (2.0 g, 11.6 mmol), 1-iodo-4-methoxybenzene (5.97 g, 25.5 mmol), KOH (5.1 g, 90.5 mmol), CuCl (0.05 g, 0.5 mmol) and 1,10-phenanthroline monohydrate (0.1 g, 0.5 mmol) were dissolved in anhydrous toluene. After being degassed by argon for 20 min, the reaction mixture was heated at 120 °C overnight. Then the mixture was cooled to room temperature. Excessive KOH was neutralized by water. After that, the mixture was extracted by dichloromethane (DCM). The organic layer was dried over anhydrous sodium sulphate (Na₂SO₄) and concentrated by evaporation. The crude product was purified by silica gel chromatography using a mixture of hexane and DCM as eluent to obtain product as a white crystal (2.5 g, 56%). Into a Schlenk flask, this purified white crystal (2.5 g, 6.5 mmol) was mixed with diborane pinacol ester (2.5 g, 9.8 mmol), KOAc (1.9 g, 19.6 mmol) and Pd(dppf)Cl₂ (1.2 g, 1.6 mmol) in 50 mL dimethylformamide (DMF). Then, the mixture was heated overnight at 80 °C. After cooling to RT, the reaction mixture was extracted by

chloroform (CF) and water. Subsequently, it was dried over anhydrous Na_2SO_4 and then concentrated by evaporation. The residue was purified by silica gel chromatography using a mixture of hexane and DCM as eluent to obtain product as a white crystal (1.8 g, 64%). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 7.53 (d, J = 7.2 Hz, 2H), 6.98 (m, 4H), 6.78-6.74 (m, 6H), 3.72 (s, 6H), 1.24 (s, 12H). ^{13}C NMR (CDCl_3 , ppm): δ 156.23, 151.33, 140.35, 135.74, 127.18, 118.68, 114.69, 83.41, 55.48, 24.86.

3.3.3. Synthesis of *TPA-OA-TPA*

In a round bottom flask 2,9-dibromo- N,N' -di(2-ethylhexyl)quinacridone (150 mg, 0.216 mmol), 4-methoxy- N -(4-methoxyphenyl)- N -(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (233 mg, 0.54 mmol), and 2 M aqueous K_2CO_3 solution (9 mL) were dissolved in degassed toluene (18 mL). The solution was purged with argon for 30 minutes, then tetrakis(triphenylphosphine)palladium (13 mg 0.011 mmol) was added. The reaction was stirred at 110 °C for 2 days. After the reaction mixture was cooled to room temperature and extracted with chloroform and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated by evaporation. The crude product was purified through column chromatography (SiO_2 , hexane: chloroform = 1:2). Reddish powder was then washed by hot acetone to afford title compound (150 mg, 61%). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 8.86 (s, 2H), 8.76 (s, 2H), 7.95-7.93 (d, J = 14.4 Hz, 2H), 7.62-7.55 (m, 6H), 7.09 (m, 12H), 6.87-6.85 (d, J = 12.6 Hz, 8H), 4.56 (m, 4H), 3.83 (s, 12H), 2.22 (m, 2H), 1.55-1.23 (m, 16H), 1.01-0.98 (t, J = 10.2 Hz, 6H), 0.87-0.83 (t, J = 10.8 Hz, 6H). ^{13}C NMR (CDCl_3 , ppm): δ 178.01, 155.95, 141.65, 135.99, 132.59, 127.02, 126.83, 126.68, 125.85, 124.35, 121.27, 120.86, 115.98, 114.87, 114.80, 114.71, 114.37, 55.52, 49.68, 38.36, 30.96, 28.77, 24.37, 23.06, 13.99, 11.22.

4. Conclusion

A novel molecular design based on the highly stable and inexpensive quinacridone dye as an electron accepting functional conjugated backbone with methoxy substituted triphenyl amine donor has been reported. The quinacridone synthesized contains bulky end capping moieties which hinder the aggregation tendency of quinacridone derivatives, inspired in the propeller molecular design reported by C. Wang. Furthermore, the addition of the bulky end capping methoxy-triphenylamine groups further extend the conjugated backbone of the molecule, possibly increasing the charge mobility of the molecule and red-shifting its emission towards the red colour band. Furthermore, the extended size of the designed molecule results in increased thermal stability when compared to the core quinacridone molecule. The OLED device results show that **TPA-QA-TPA** is an effective red dopant in the common host material Alq₃. This paves the way for further research in QA based materials as red dopant materials and device optimization to enhance efficiencies. Further work in the mentioned areas are ongoing in our laboratory.

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