Dyes and Pigments 101 (2014) 261-269

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis and electrochemical properties of symmetric squarylium dyes containing diarylamine



PIGMENTS

Yutaka Ohsedo^{a,*}, Misao Miyamoto^{a,b,1}, Akihiro Tanaka^b, Hisayuki Watanabe^{a,b}

^a Advanced Materials Research Laboratory, Collaborative Research Division, Art, Science and Technology Center for Cooperative Research, Kyushu University, 4-1 Kyudaishinmachi, Nishi-ku, Fukuoka 819-0388, Japan

^b Nissan Chemical Industries, Ltd., 2-10-1 Tsubonishi, Funabashi, Chiba 274-8507, Japan

ARTICLE INFO

Article history: Received 17 May 2013 Received in revised form 22 September 2013 Accepted 30 September 2013 Available online 19 October 2013

Keywords: Squarylium dyes Electrochemical properties Radical cation Dication

1. Introduction

Squaraine dyes or squarylium dyes (SQDs) are a well-known family of functional dyes to be used as colouring materials [1], photoconductive materials in photocopiers [2] and the active layer in optical memory such as digital versatile discs [3]. In this decade, SQDs have been studied as a core block of active materials for new types of organic electroactive and photoactive devices such as electroluminescent devices [4], bulk heterojunction organic photovoltaic cells [5], and dye-sensitized solar cells [6]. In the field of medicinal science, SQDs with near-infrared absorption properties have been studied as a fluorophore for sensing materials [7] and a sensitizer for photodynamic therapy [8]. Moreover, SQDs have attracted attention as unique colourants of π -conjugate units for supramolecular ion sensing [9], foldarmer formation [10], extended π -conjugate compounds [11] such as low bandgap polymers for organic conductors [12], π -extended systems such as bissquarylium compounds [13], and squarylium oligomers [14]. Thus, SQDs are considered unique units of π -conjugate dyes for the various applications mentioned above, and their unique reactivity

E-mail addresses: ohsedo@astec.kyushu-u.ac.jp, twopolaron@yahoo.co.jp (Y. Ohsedo).

ABSTRACT

We studied the synthesis and electrochemical properties of symmetric squarylium dyes (SQDs) containing diarylamine with various structures. It was shown that several of our synthesized SQDs had improved electrochemical properties and might be a promising and an easy modifiable π -conjugate core block of active materials for electroactive and photoactive devices.

© 2013 Elsevier Ltd. All rights reserved.

[15] and capacity for supramolecular modification in high durability applications in the field of medicine [16] have been explored. Although the previously discussed SQDs have been extensively studied, they absorb primarily in the visible to near-infrared regions. New SQDs that absorb in the blue laser region (\sim 405 nm) are needed for new applications in which blue lasers are used, such as active materials for optical memory or sensitizers for photochemical reactions.

Recently, for their usefulness in well-defined molecular structure designs, π -conjugate compounds have garnered much attention as candidates for active materials of organic electroactive and photoactive devices. Better electrochemical properties of the π conjugate compounds, such as electrochemical reversibility, might be needed in the active materials for rechargeable batteries [17]. On the other hand, better electrochemical reversibility of π -conjugate compounds, both transporting materials and emitting materials, in electroluminescent devices might be considered essential for designing high-performance π -conjugate compounds [18]. The electrochemical reversibility may become necessary as better design criteria emerges for electroactive and photoactive materials.

To develop SQDs as potential blue-laser absorption dyes and as promising candidates for the core block of functional dyes, we have studied the synthesis and electrochemical properties of symmetric SQDs containing diarylamine with blue light absorption (Scheme 1). These compounds can be synthesized in a one-step reaction with



^{*} Corresponding author. Tel.: +81 92 400 4381; fax: +81 92 400 4382.

¹ Current address: Nippon Phosphoric Acid Co., JP, 14 Kitasode, Sodegaura, Chiba, Japan.

^{0143-7208/\$ -} see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2013.09.047



Scheme 1. Chemical structures of symmetric SQDs.

easy workup from squaric acid and secondary arylamine. It was shown that several of our extended SQDs have and better electrochemical reversibility than primitive SQDs and might be a promising π -conjugate core block of an active material for electroactive and photoactive devices using blue laser or other lasers for applications mentioned above. Further modification of arylamine as a raw reagent will offer the versatility for creating new symmetric SQDs with high performance based on this study.

Related to this paper, the synthesis [19] and electrochemical properties [20] of primitive SQDs containing diarylamine (MePhA-SQ and DPhA-SQD) were reported. The previous studies have primarily focused on analysis of the chemical structure of primitive SQDs, including dialkylamine and diarylamine. The electrochemical properties such as reversibility of other extended symmetric-type SQDs are reported here for the first time.

2. Experimental section

2.1. General

Dichloromethane (super dehydrated), *N*,*N*-dimethylformamide (Spectrosol[®], DOJINDO Laboratories) and squaric acid were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. All other reagents and solvents were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K).

¹H NMR and ¹³C NMR were recorded on an AVANCE 500 (500 MHz, Bruker BioSpin K.K.) spectrometer. MALDI–TOF MS was performed with an autoflex III (Bruker Daltonics Inc.) using sinapinic acid as a matrix. Elemental analysis was performed with a Yanaco CHN corder MT-5 (Yanaco New Science Inc.). Single-crystal X-ray diffraction data were recorded on a SMART APEX II Ultra X-ray diffractometer (Bruker AXS K.K.) with CuK α at -50 °C. Crystal structures were visualised from CIF data using Mercury (Cambridge Crystallographic Data Centre). Electrochemical measurements were carried out with an electrochemical analyzer model 708c (CH Instruments, Inc.). Electronic absorption spectra within the ultraviolet–visible region were measured with a V-670 UV–vis spectrophotometer (JASCO Corporation) by using a 10 mm path length

of a quartz glass cell (concentration of a measured SQD solution: ${\sim}1\times10^{-6}$ M).

2.2. Synthesis of SQDs

2.2.1. MePhA-SQD

Under N₂ atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], N-methylaniline (3.00 g, 27.4 mmol), and squaric acid (1.28 g, 11.2 mmol) were combined and stirred at 110 °C for 21 h, then cooled to room temperature. The obtained precipitate was filtered, washed with methanol and dried in vacuo to yield an orange powder (2.95 g, yield 90.8%). ¹H NMR (500 MHz, DMSO-*d*6, TMS, δ , ppm): 7.22 (m, 8H, Ar–H), 7.29 (m, 2H, Ar–H at the para position), 3.84 (s, 6H, N–CH₃). ¹³C NMR (125 MHz, CDCl₃, TMS, δ , ppm): 177.47, 168.52, (141.24, 141.09), 129.24, 127.27, 123.00, (39.19, 38.73). MALDI–TOF MS: calcd for C₁₈H₁₆N₂O₂ (MW = 292.12): *m*/*z* = 292.61 [M⁺]. Elemental anal. calcd for C₁₈H₁₆N₂O₂: C, 73.95%; H, 5.52%; N, 9.58%. Found: C, 73.93%; H, 5.59%; N, 9.66%. It is worth noting that in ¹³C NMR spectrum of MePhA-SQD might show peaks based on conformers as shown in the literature describing squalyrium dyes [21].

2.2.2. DPhA-SQD

Under N₂ atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], diphenylamine (3.00 g, 17.6 mmol), and squaric acid (809 mg, 7.09 mmol) were combined and stirred at 110 °C for 21 h, then cooled to room temperature. The obtained precipitate was filtered, washed with methanol and dried in vacuo to yield an orange powder (1.73 g, yield 58.5%). ¹H NMR (500 MHz, DMSO-*d*6, TMS, δ , ppm): 7.44 (t, 8H, *J* = 7.7 Hz, Ar–H), 7.35 (t, 4H, *J* = 7.3 Hz, Ar–H at the para position), 7.25 (d, 8H, *J* = 7.6 Hz, Ar–H). ¹³C NMR (125 MHz, CDCl₃, TMS, δ , ppm): 178.82, 168.09, 140.44, 128.94, 127.67, 125.43. MALDI–TOF MS: calcd for C₂₈H₂₀N₂O₂ (MW = 416.15): *m*/*z* = 416.82 [M⁺]. Elemental anal. calcd for C₂₈H₂₀N₂O₂: C, 80.75%; H, 4.84%; N, 6.73%. Found: C, 80.62%; H, 4.79%; N, 6.78%.

2.2.3. NpPhA-SQD

Under N₂ atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], *N*-methylaniline (4.81 g, 21.3 mmol), and squaric acid (1.00 g, 8.77 mmol) were combined and stirred at 110 °C for 25 h, then cooled to room temperature. The obtained precipitate was filtered,



Scheme 2. Reaction scheme of symmetric SQDs containing arylamines.

washed with methanol and dried in vacuo to yield an orange powder (3.55 g, yield 78.4%). ¹H NMR (500 MHz, DMSO-*d*6, TMS, δ , ppm): 7.82 [s (br), 6H, Ar-H], 7.71 [s (br), 2H, Ar-H], 7.48 [s (br), 4H, Ar-H], 7.43 (m, 12H, Ar-H). ¹³C NMR (125 MHz, CDCl₃, TMS, δ, ppm): 179.40, 168.68, 140.93, 138.21, 133.45, 132.82, 129.41, 128.69, 128.15, 127.25, 127.07, 125.91, 124.54, 123.84. MALDI-TOF MS: calcd for $C_{36}H_{24}N_2O_2$ (MW = 516.18): m/z = 516.93 [M⁺]. Elemental anal. calcd for C₃₆H₂₄N₂O₂: C, 83.70%; H, 4.68%; N, 5.42%. Found: C, 83.60%; H, 4.71%; N, 5.49%. In the ¹³C NMR spectrum of NpPhA-SOD, although 16 peaks were expected on the basis of the chemical structure, only 14 peaks were observed. When the DEPT-135 ¹³C NMR spectrum of NpPhA-SQD in CDCl₃ was obtained, six peaks attributable to quaternary carbons disappeared i.e., the peaks at 179.40, 168.68, 140.93, 138.21, 133.45, and 132.82 may have coincided with those of quaternary carbons; therefore, the remaining eight peaks may contain the two lost CH peaks.

2.2.4. DTolA-SQD

Under N₂ atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], p,p'ditolylamine (2.00 g, 9.83 mmol), and squaric acid (463 mg, 4.06 mmol) were combined and stirred at 110 °C for 30 h, then cooled to room temperature. The obtained precipitate was filtered, washed with methanol and dried in vacuo to yield a yellow powder (1.42 g, yield 74.1%). ¹H NMR (500 MHz, DMSO-*d*6, TMS, δ , ppm): 7.22 (t, 8H, *J* = 8.2 Hz, Ar–H), 7.09 (t, 8H, *J* = 8.5 Hz, Ar–H), 2.33 (s, 12H, –CH₃). ¹³C NMR (125 MHz, CDCl₃, TMS, δ , ppm): 178.21, 168.78, 138.62, 137.84, 129.88, 125.56, 21.49. MALDI–TOF MS: calcd for C₃₂H₂₈N₂O₂ (MW = 472.22): *m*/*z* = 472.90 [M⁺]. Elemental anal. calcd for C₃₂H₂₈N₂O₂: C, 81.33%; H, 5.97%; N, 5.93%. Found: C, 81.30%; H, 5.94%; N, 6.00%.

2.2.5. MeOPhTolA-SQD

Under N₂ atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], 4-methoxy-4'-methyldiphenylamine (2.00 g, 9.19 mmol) and



Fig. 2. Electronic absorption spectra of SQDs in the DMF solution.

squaric acid (428 g, 3.75 mmol), were combined and stirred at 110 °C for 17 h, then cooled to room temperature. The obtained precipitate was filtered, washed with methanol and dried in vacuo to yield a yellow powder (1.46 g, yield 77.2%). ¹H NMR (500 MHz, DMSO-*d*6, TMS, δ , ppm): 7.41 (d, 4H, *J* = 8.5 Hz, Ar–H), 7.15 (d, 4H, *J* = 8.8 Hz, Ar–H), 7.08 (d, 4H, *J* = 8.2 Hz, Ar–H), 6.96 (d, 4H, *J* = 8.8 Hz, Ar–H), 3.79 (s, 6H, –OCH₃), 2.33 (s, 6H, –CH₃). ¹³C NMR (125 MHz, CDCl₃, TMS, δ , ppm): 177.65, 168.89, 159.20, 138.74, 137.77, 134.18, 129.88, 127.01, 125.35, 114.49, 55.88, 21.50. MALDI–TOF MS: calcd for C₃₂H₂₈N₂O₄ (MW = 504.20): *m*/*z* = 504.88 [M⁺]. Elemental anal. calcd for C₃₂H₂₈N₂O₄: C, 76.17%; H, 5.59%; N, 5.55%. Found: C, 76.45%; H, 5.43%; N, 5.65%.

2.3. Measurements

Cyclic voltammetry for N₂ purged dichloromethane solutions of the SQDs (1.0×10^{-3} mol dm⁻³) containing *n*-Bu₄NClO₄ (0.1 mol dm⁻³) was conducted with a platinum disk (1.6 mm in diameter), platinum wire, and Ag/Ag⁺ (0.01 mol dm⁻³) as the working, counter and reference electrodes, respectively. Under same conditions, the ferrocene/ferrocenium (Fc/Fc⁺) potential ($E_{1/2}$) showed 0.07 V vs. Ag/Ag⁺ (0.01 mol dm⁻³).

2.4. Molecular modelling

For the density function theory (DFT) calculations of the absorbance wavelength of SQDs, we conducted conformational



Fig. 1. Crystal structures of SQDs: (a) DPhA-SQD and (b) DTolA-SQD. Small ball, hydrogen.

264

 Table 1

 Optical properties for SQDs in the DMF solution and results of calculations.

Dye	λ_{max}/nm	$\log \epsilon$	λ_{max}/nm (calc.)
MePh-SQD	387	4.60	395
DPhA-SQD	411	4.59	400
NpPhA-SQD	423	4.55	426
DTolA-SQD	415	4.67	404
MeOPhTolA-SQD	418	4.67	424

searches using MMFF94s (CONFLEXTM) and performed structural optimizations of the ground state of SQDs using B3LYP/6-31G (d) ("Firefly" – a freely available ab initio and DFT computational chemistry program). Estimations of the UV–vis spectra were calculated using TD-B3LYP/6-31G(d) ("Firefly"). In the DFT calculations of the frontier molecular orbitals (HOMO and LUMO) of SQDs, conformational searches were conducted using MMFF94s

(CONFLEXTM) and structural optimizations were conducted using B3LYP/6-31G (d) ("Firefly").

3. Results and discussions

Symmetric-type SQDs containing a diarylamine moiety, MePhA-SQD, DPhA-SQD, NpPhA-SQD, DTolA-SQD, and MeOPhTolA-SQD (Scheme 1) were synthesized from the dehydration reaction of squaric acid and corresponding secondary arylamine in toluene/*n*-butanol as solvents with reflux (Scheme 2). Crude SQDs were filtered and washed with methanol several times, and the resultant SQDs, obtained without a tedious purification process such as column chromatography, showed sufficiently high purity in the elemental analysis. These SQDs were soluble in CHCl₃, dichloromethane, DMF, and DMSO. In the synthesis of SQDs, we demonstrated a





Fig. 3. Cyclic voltammograms of SQDs in dichloromethane containing n-Bu₄NClO₄ (0.1 mol dm⁻³): (a) MePh-SQD, (b) DPhA-SQD, (c) NpPhA-SQD, (d) DTolA-SQD and (e) MeOPhTolA-SQD. Red lines, one-electron anodic oxidation process; blue lines, two-electron anodic oxidation process. The sweep rate was 0.1 V s⁻¹.

Table 2 Oxidation potentials of the SQDs [V vs. Ag/Ag^+ (0.01 mol $dm^{-3})].$

Samples	First wave		Second wave			
	$E_{\rm pa}$	Epc	$I_{\rm pc}/I_{\rm pa}$	Epa	Epc	$I_{\rm pc}/I_{\rm pa}$
MePh-SQD	0.88	0.77	0.96	1.42	_	_
DPhA-SQD	0.95	0.85	0.93	1.50	_	_
NpPhA-SQD	0.93	0.82	0.94	1.35	_	_
DTolA-SQD	0.86	0.75	1.00	1.31	1.18	1.35
MeOPhTolA-SQD	0.79	0.68	0.99	1.20	1.07	1.11

 E_{pa} , peak anodic oxidation potential; E_{pc} , peak anodic oxidation.

 I_{pc}/I_{pa} was estimated by Nicholson's equation [24,25] (see ESI). The sweep rate was 0.1 V s^{-1}.

The sweep rate was 0.1 V s^{-1} .

suitable method for the synthesis and workup of SQDs using secondary arylamines whose nucleophilic ability is hindered by aryl groups. Related to these results, same kind of simple purification processes on other squarylium compounds was reported in literature [22].

To clarify the chemical structure of the SQDs, analysis of their crystal structures was attempted by X-ray diffraction (XRD). Unfortunately, the crystals suitable for XRD were unable to obtain without DPhA-SQD and DTolA-SQD. Fig. 1 shows the ball-and-stick images of DPhA-SQD and DTolA-SQD obtained from XRD analysis (see also Supplementary data) [23]. It was shown that the arylamine moieties were connected not to the 1- and 2-positions but to the 1- and 3-positions of the cyclobutane ring. In the obtained

crystal structures, the diphenylamine moiety of DPhA-SQD and DTA-SQD showed propeller-like conformations, as shown in the crystal structures of π -conjugated compounds containing triphenylamine [24] or diphenylamine moieties [25]. We supposed the same type of arylamine connection to the cyclobutane ring in other SQDs in this study because SQDs showed λ_{max} in a similar wavelength region, as in the following results. These propeller-like connections of phenyl rings make the λ_{max} of SQDs are shorter compared to those of general SQDs, probably because of decreased π -conjugation. On comparing the XRD results for our system with those of 1,3-bis(dimethylamino)-3-cyclobutene-2,4-dione, the *N*-methylated analogue are coplanar [26]; the distinct feature of our SQDs containing arylamine is their propeller-like structures.

Fig. 2 shows the absorption spectra of the SQDs, and Table 1 lists their optical properties. The differences in λ_{max} reflect the relationship between the extent of π -conjugation in SQDs and their chemical structures. Whereas ordinary SQDs showed light absorption among the deep visible and near infrared with strong molecular extinction coefficients, these symmetric SQDs with arylamines exhibit absorption at a shorter visible region (~400 nm) because the peri-position hydrogen atoms of arylamines hinder π -conjugation, as indicated by crystal analysis showing the existence of SQD propeller structures. From Table 1, the red shift in λ_{max} reflects the increase in π -conjugation of SQDs: on the basis of MePhA-SQD (λ_{max} : 387 nm), substitution from methyl to phenyl (λ_{max} : 411 nm) and the naphthyl group (λ_{max} :



Fig. 4. The frontier molecular orbitals of SQDs obtained by DFT calculations.



Fig. 5. The relationship between calculated and electrochemically estimated HOMO of SQDs.

423 nm) increased the π -conjugation (the naphthyl group showed more π -conjugation than the phenyl group), and on the basis of DPhA-SQD (λ_{max} : 411 nm), substitution from H- to methyl (λ_{max} : 415 nm) and the methoxy group (λ_{max} : 418 nm) contributed to the π -conjugation by substituent effect (the methoxy group might support better π -conjugation than the methyl group by stronger resonance effect). From these results and $\log \epsilon$, SODs in this study have similar π -conjugation lengths; thus, they have symmetric structures connected with the 1- and 3-positions of the cyclobutane ring, as envisioned. Whereas the DFT calculations of the λ_{max} values of the SQDs were conducted under the assumption of gas-phase molecules, the λ_{max} results of the samples in DMF coincided better with the calculated results, to within 10 nm. This agreement between the calculated and experimental results was probably because of the formation of ideal π -conjugation in the SQDs in DMF.

Next, we examine the electrochemical properties of the SQDs. The electrochemical measurements of SQD dichloromethane solutions were carried out by cyclic voltammetry. Fig. 3 shows cyclic voltammograms for the anodic oxidation process of SQDs, and Table 2 lists the electrochemical parameters of SQDs [27,28]. Whereas the one-electron anodic oxidation process of MePh-SQD, DPhA-SQD, and NpPhA-SQD in dichloromethane displayed high reversibility ($I_{pc}/I_{pa} = \sim 1$, but with wider $E_{pa} - E_{pc} = \sim 100$ mV), the two-electron anodic oxidation processes for these SQDs were irreversible. A second anodic wave ascribable to the two-electron oxidation of the SQDs was observed, but the corresponding cathodic waves were much weaker in intensity [Fig. 2(a)–(c)].

Table 3		
HOMO, LUMO, and bandgap obtained by	y DFT calculations and ex	perimental results

Samples	HOMO/ eV	LUMO/ eV	E _{bg} / eV ^a	E _{obg} (onset/nm)/ eV ^b	HOMO _{ec} / eV ^c
MePh-SQD DPhA-SQD NpPhA-SQD DToIA-SQD MeOPhToIA- SQD	-5.09 -5.00 -4.96 -4.82 -4.67	-1.68 -1.66 -1.77 -1.50 -1.38	3.41 3.34 3.19 3.32 3.29	2.86(433) 2.77(448) 2.67(465) 2.75(451) 2.71(457)	-6.11 -6.18 -6.16 -6.09 -6.02

HOMO_{ec} [eV] = E_{pa} - 0.07 - 5.30. "0.07" means 0.07 V vs. Ag/Ag⁺ (0.01 mol dm⁻³). A rough assumption on neglecting solvent effects provides F_c/F_c^+ = -5.30 eV from vacuum level [28].

^a $E_{\rm g}$ (bandgap energy from calculation) was |HOMO – LUMO|.

 $^{\rm b}$ $\ddot{E}_{\rm obg}$ (optical bandgap energy) was estimated by onset wavelength at longer absorption region.

 $^{\rm c}\,$ HOMO_{\rm ec} (electrochemically obtained HOMO) were estimated by using following equation.



Fig. 6. Cyclic voltammograms of DToIA-SQD in dichloromethane containing *n*-Bu₄N-ClO₄ (0.1 mol dm⁻³): (a) two-electron anodic oxidation process and (b) one-electron anodic oxidation process. The sweep rates were from 0.05 to 0.4 V s⁻¹.

When the scan was repeated ten times in one-electron anodic oxidation, no new peaks were observed. This suggests that the radical cations on the SQDs were chemically stable under these conditions. Compared with the E_{pa} of MePh-SQD, DPhA-SQD and NpPhA-SQD, MePh-SQD with lower λ_{max} showed lower E_{pa} . This may be ascribable to the hyperconjugation of the methyl group in MePh-SQD. The results for MePhA-SQ and DPhA-SQD corresponded well to those in the literature [20]. In contrast, DToIA-SQD and MeOPhTolA-SQD in dichloromethane underwent two electron oxidations and showed high reversibility $[I_{pc}/I_{pa} = 1$ (for MeOPhTolA-SQD and the first wave of DTolA-SQD), but with wider $E_{\rm pa} - E_{\rm pc} = \sim 100 \text{ mV}$], showing two anodic waves, and two corresponding cathodic waves in their cyclic voltammograms corresponding to a two-electron oxidation process [Fig. 3(d) and (e)]. When the scan was repeated, no new definite anodic and cathodic waves attributable to the formation of the corresponding SOD dimer were observed. This suggests that the radical cation and dication on the SQDs were chemically stable under these conditions. The difference in stability improvement between electrochemical species of DToIA-SQD and MeOPhToIA-SQD in the second waves $(I_{pc}/I_{pa} \text{ in Table 2})$ might be attributable to the difference in the inductive effect between the methyl and methoxy group on π conjugation of SQDs, which tended to stabilize the radical cation and dication. Because of the overestimation of the second wave cathodic current of DToIA-SQD and MeOPhToIA-SQD due to the difficulty of clear division from the third wave, the I_{pc}/I_{pa} value might contain current from the third wave. These results indicate that the stability of the SQD radical cation and dication was enhanced by the increased π -conjugation length of the SQD moiety by substituting the hydrogen atoms with the methyl and methoxy group. Because of the extended π -conjugation and resulting charge



Fig. 7. Cyclic voltammograms of MeOPhTolA-SQD in dichloromethane containing *n*-Bu₄NClO₄ (0.1 mol dm⁻³): (a) two-electron anodic oxidation process and (b) one-electron anodic oxidation process. The sweep rates were from 0.05 to 0.4 V s⁻¹.

delocalization, the coupling reaction of the SQD radical cations that could give rise to the corresponding dimer moieties did not take place.

By conducting DFT calculations of the frontier molecular orbitals of SQDs, we determined the shape of the HOMO and LUMO of SQDs (Fig. 4). As shown in Fig. 4, the HOMO and LUMO of the SQDs are located primarily at the cyclobutane ring and at the two adjacent N atoms in the planar figures. This compact and planar π -conjugation of diarylamine SQDs might make the λ_{max} of these SQDs shorter than that of general SQDs. This propeller-like geometry of SQDs obtained from the DFT calculations is shown in Fig. 4 which corresponds well with the SQDs' XRD results as shown in Fig. 1. In Table 3, the bandgap energies obtained from both calculations and absorption bands (E_{bg} and E_{obg} , respectively) and the electrochemically obtained HOMO (HOMOec) are listed. As shown in Table 3, although the calculation results for the HOMOs of the SQDs that correspond to the oxidation potentials tend to increase in value in accordance with the π -conjugation length (λ_{max}), the experimental cyclic voltammetry results for the SQDs differ to some extent. The E_{bg} values are larger than the E_{obg} values; however, the $E_{\rm bg}$ values showed the same tendency as the $E_{\rm obg}$ values. The calculated HOMOs were ca. 1 eV lower than the corresponding HOMO_{ec} values, although both HOMOs were linearly correlated, except for those of MePhA-SQD, as shown in Fig. 5. The deviation of the HOMOs of MePhA-SQD from linearity is probably because of steric hindrance around the N atoms of MePhA-SQD during the electrochemical oxidation process. The shape of the π -electron orbitals of the HOMO and their surroundings, which include their steric circumstances are considered to affect the extraction of electrons from dyes during electrochemical processes. In the electrochemical oxidation process of diarylamine SQDs, given the deviation of the HOMO, an electron may be extracted from electron-donating N atoms (amine) rather than from the electron-accepting cyclobutane-carbonyl moiety; therefore, the steric hindrance around N atoms might hamper the extraction of an electron during electrochemical oxidation. This hindrance may explain why the $E_{\rm pa}$ of MePhA-SQD is lower than that of DPhA-SQD despite its lower π -conjugation length, as determined from the experimental (absorption) and calculation results. MePhA-SQD exhibited an $E_{\rm pa}$ lower than that of DPhA-SQD because of its lower steric hindrance around N atoms, which resulted in the deviation from linearity between the HOMO_{ec} and the calculated HOMO shown in Fig. 5.

To further investigate the electrochemical reversibility of SQDs, the sweep rates were changed. Figs. 6 and 7 show the one- and two-electron anodic oxidation processes of DToIA-SQD and MeOPhToIA, respectively. It is known that linearity in the square root of the sweep rate vs. current and constant oxidation potentials during sweep rate changes are criteria for electrochemical reversibility [27]. Whereas the increase in current was linear in the square root of sweep rate vs. current, the oxidation potentials slightly shifted to higher values with increasing sweep rates. In addition, it is showed that small shoulder peaks were observed in two electron oxidation in around 0.8 V vs. Ag/Ag⁺ (Figs. 6(a) and 7(a)). From these results, symmetric SQDs containing diarylamine showed pseudo-electrochemical reversibility and chemical reversibility in the anodic oxidation process.

4. Conclusions

We have studied the synthesis and electrochemical properties of symmetric SQDs containing diarylamine for developing blue laser absorption dyes and core block of functional dyes. These SQDs were synthesized in a one-step dehydration reaction from squaric acid and secondary arylamine with a simple workup. The SOD chemical structures determined by XRD analysis had arylamine moieties symmetrically connected to the 1- and 3-positions of the cyclobutane ring. From electrochemical measurements in the anodic oxidation process, these SQDs showed one- and/or two-electron oxidation with pseudo-electrochemical reversibility and chemical reversibility. These results suggest that symmetric SQDs containing diarylamine might be a new family of promising candidates of active materials for electroactive and photoactive devices. Because secondary arylamines, which are raw materials of SQDs in this study, are easily modified and extended by such wellestablished chemical reactions as the arylamine synthesis by Buchwald–Hartwig amination [29], symmetric SQDs containing arylamine with further higher electrochemical performance can be designed and easily synthesized on the basis of our results.

Acknowledgements

We would like to thank Nissan Chemical Industries for financial and technical support and Dr. Osamu Hirata and Dr. Fumiyasu Ono for their helpful discussions and comments. We are grateful to the Service Centre of the Elementary Analysis of Organic Compounds, Kyushu University for the elemental analysis. A part of this work was supported by the Nanotechnology Network Project (Kyushuarea Nanotechnology Network) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. We would like to thank Enago (www.enago.jp) for the English language review.

Appendix A. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.09.047.

References

- (1) (a) Fabian J, Nakazumi H, Matsuoka M. Near-infrared absorbing dyes. Chem Rev 1992;92:1197–226;
 (b) Zollinger H. Color chemistry. 3rd ed. Verlag Helvetica Chimica Acta and
- WILEY-VCH; 2003.
- [2] Law KY. Organic photoconductive materials: recent trends and developments. Chem Rev 1993;93:449–68.
- [3] Emmelius M, Pawlowski G, Vollmann HW. Materials for optical data storage. Angew Chem Int Ed 1989;28:1445–600.
 [4] (a) Matui M, Tanaka S, Funabiki K, Kitaguchi T. Synthesis, properties, and
- [4] (a) Matui M, Tanaka S, Funabiki K, Kitaguchi T. Synthesis, properties, and application as emitters in organic electroluminescence devices of quinacridone- and squarylium-dye-centered dendrimers. Bull Chem Soc Jpn 2006;79: 170–6;

(b) Smits ECP, Setayesh S, Anthopoulos TD, Buechel M, Nijssen W, Coehoorn R, et-al. Near-infrared light-emitting ambipolar organic field-effect transistors. Adv Mater 2007;19:734–8.

[5] (a) Silvestri F, Irwin MD, Beverina L, Facchetti A, Pagani GA, Marks TJ. Efficient squaraine-based solution processable bulk-heterojunction solar cells. J Am Chem Soc 2008;130:17640–1;

(b) Mayerhöffer U, Deing K, Gruss K, Braunschweig H, Meerholz K, Würthner F. Outstanding short-circuit currents in BHJ solar cells based on NIR-absorbing acceptor-substituted squaraines. Angew Chem Int Ed 2009;48: 8776–9;

(c) Bagnis D, Beverina L, Huang H, Silvestri F, Yao Y, Yan H, et-al. Marked alkylvs alkenyl-substituent effects on squaraine dye solid-state structure, carrier mobility, and bulk-heterojunction solar cell efficiency. J Am Chem Soc 2010;132:4074–5;

(d) Xiao X, Wei GD, Wang SY, Zimmerman JD, Renshaw CK, Thompson ME, etal. Small-molecule photovoltaics based on functionalized squaraine donor blends. Adv Mater 2012;24:1956–60.

[6] (a) Sayama K, Tsukagoshi S, Mori T, Hara K, Ohga Y, Shinpou A, et-al. Efficient sensitization of nanocrystalline TiO₂ films with cyanine and merocyanine organic dyes. Sol Energy Mater Sol Cells 2003;80:47–71;

(b) Yum JH, Walter P, Huber S, Rentsch D, Geiger T, Nüesch F, et-al. Efficient far red sensitization of nanocrystalline TiO_2 films by an unsymmetrical squaraine dye. J Am Chem Soc 2007;129:10320;

(c) Geiger T, Kuster S, Yum JH, Moon SJ, Nazeeruddin MK, Grätzel M, et-al. Molecular design of unsymmetrical squaraine dyes for high efficiency conversion of low energy photons into electrons using TiO_2 nanocrystalline films. Adv Funct Mater 2009;19:2720–1;

(d) Nakao H, Maeda T, Nakazumi H. Near-infrared-absorbing π -extended squarylium-based dyes with dicyanovinylene substitution for dye-sensitized solar cell applications. Chem Lett 2013:25–7:

(e) Maeda T, Tsukamoto T, Seto A, Yagi S, Nakazumi H. Synthesis and characterization of squaraine-based conjugated polymers with phenylene linkers for bulk heterojunction solar cells. Macromol Chem Phys 2012;213: 2590–7.

[7] (a) Patonay G, Salon J, Sowell J, Strekowski L. Noncovalent labeling of bio-molecules with red and near-infrared dyes. Molecules 2004;9:40–9;
(b) Luo SL, Zhang EL, Su YP, Cheng TM, Shi CM. A review of NIR dyes in cancer targeting and imaging. Biomaterials 2011;32:7127–38;
(c) Nakazumi H, Colyer CL, Kaihara K, Yagi S, Hyodo Y. Red luminescent

squarylium dyes for noncovalent HSA labeling. Chem Lett 2003:804–5; (d) Umezawa K, Citterio D, Suzuki K. Water-soluble NIR fluorescent probes based on squaraine and their application for protein labeling. Anal Sci 2008:24:213–7:

(e) Yuan L, Lin WY, Zheng KB, He LW, Huang WM. Far-red to near infrared analyte-responsive fluorescent probes based on organic fluorophore plat-forms for fluorescence imaging. Chem Soc Rev 2013;42:622–61.

[8] (a) Beverina L, Crippa M, Landenna M, Ruffo R, Salice P, Silvestri F, et-al. Assessment of water-soluble π-extended squaraines as one- and two-photon singlet oxygen photosensitizers: design, synthesis, and characterization. J Am Chem Soc 2008;130:1894–902;

(b) Avirah RR, Jayaram DT, Adarsh N, Ramaiah D. Squaraine dyes in PDT: from basic design to in vivo demonstration. Org Biomol Chem 2012;10:911–20.
[9] (a) Ros-Lis JV, Marcos MD, Mártinez-Máňez R, Rurack K, Soto J. A regenerative

[9] (a) Ros-Lis JV, Marcos MD, Martinez-Máñez R, Rurack K, Soto J. A regenerative chemodosimeter based on metal-induced dye formation for the highly selective and sensitive optical determination of Hg²⁺ ions. Angew Chem Int Ed 2005;44:4405–7;

(b) Rostami A, Wei CJ, Guérin G, Taylor MS. Anion detection by a fluorescent poly(squaramide): self-assembly of anion-binding sites by polymer aggregation. Angew Chem Int Ed 2011;50:2059–62.

[10] (a) Ajayaghosh A, Arunkumar E, Daub J. A highly specific Ca²⁺ ion sensor: signaling by exciton interaction in a rigid-flexible-rigid bichromophoric "H" foldamer. Angew Chem Int Ed 2002;41:1766–9;

(b) Arunkumar E, Chithra P, Ajayaghosh A. A controlled supramolecular approach toward cation-specific chemosensors: alkaline earth metal iondriven exciton signaling in squaraine tethered podands. J Am Chem Soc 2004;126:6590–8;

(c) Chithra P, Varghese R, Divya KP, Ajayaghosh A. Solvent-induced aggregation and cation-controlled self-assembly of tripodal squaraine dyes: optical, chiroptical and morphological properties. Chem Asian J 2008;3:1365–73; (d) Ajayaghosh A, Chithra P, Varghese R, Divya KP. Controlled self-assembly of squaraines to 1D supramolecular architectures with high molar absorptivity. Chem Commun 2008:969–71.

[11] For reviews: (a) Ajayaghosh A. Donor-acceptor type low band gap polymers: polysquaraines and related systems. Chem Soc Rev 2003;32:181-91; (b) Yagi S, Nakazumi H. Squarylium dyes and related compounds. Top Heterocycl Chem 2008;14:133-81; (c) Sreejith S, Carol P, Chithra P, Ajayaghosh A. Squaraine dyes: a mine of molecular materials. J Mater Chem 2008;18:264-74; (d) McEwen JJ, Wallace KJ. Squaraine dyes in molecular recognition and self-assembly. Chem Commun 2009:6339-51; (e) Beverina L, Salice P. Squaraine compounds: tailored design and synthesis

towards a variety of material science applications. Eur J Org Chem 2010: 1207–25.

- [12] (a) Ajayaghosh A. Chemistry of squaraine-derived materials: near-IR dyes, low band gap systems, and cation sensors. Acc Chem Res 2005;38:449–59;
 (b) Shi QQ, Chen WQ, Xiang JF, Duan XM, Zhan XW. A low-bandgap conjugated polymer based on squaraine with strong two-photon absorption. Macromolecules 2011;44:3759–65.
- [13] Yagi S, Fujie Y, Hyodo Y, Nakazumi H. Synthesis, structure, and complexation properties with transition metal cations of a novel methine-bridged bisquarylium dye. Dyes Pigm 2002;52:245–52.
 [14] (a) Yagi S, Nakasaku Y, Maeda T, Nakazumi H, Sakurai Y. Synthesis and near-
- (a) Yagi S, Nakasaku Y, Maeda T, Nakazumi H, Sakurai Y. Synthesis and nearinfrared absorption properties of linearly π-extended squarylium oligomers. Dyes Pigm 2011;90:211–8;
 (b) Kuster S. Geiger T. Strategies and investigations on bridging squaraine dve

(b) Kuster S, Geiger T. Strategies and investigations on bridging squaraine dye units. Dyes Pigm 2012;95:657–70.

- [15] Yang SJ, You JS, Lan JD, Gao G. Facile access to extremely efficient energy-transfer pairs via an unexpected reaction of squaraines with ketones. J Am Chem Soc 2012;134:11868–71.
 [16] (a) Arunkumar E, Forbes CC, Noll BC, Smith BD. Squaraine-derived rotax-
- [16] (a) Arunkumar E, Forbes CC, Noll BC, Smith BD. Squaraine-derived rotaxanes: sterically protected fluorescent near-IR dyes. J Am Chem Soc 2005;127:3288–9;

(b) Gassensmith JJ, Baumes JM, Smith BD. Discovery and early development of squaraine rotaxanes. Chem Commun 2009:6329–88;

 (c) Baumes JM, Gassensmith JJ, Giblin J, Lee JJ, White AG, Culligan WJ, et-al. Storable, thermally activated, near-infrared chemiluminescent dyes and dyestained microparticles for optical imaging. Nat Chem 2010;2:1025–30;
 (d) Cole EL, Arunkumar E, Xiao SZ, Smith BA, Smith BD. Water-soluble, deep-red

fluorescent squaraine rotaxanes. Org Biomol Chem 2012;10:5769–73.
(a) Nishide H, Oyaizu K. Toward flexible batteries. Science 2008;319:737–8; (b) Morita Y, Nishida S, Murata T, Moriguchi M, Ueda A, Satoh M, et-al. Organic tailored batteries materials using stable open-shell molecules with degenerate frontier orbitals. Nat Mater 2011;10:947–51; (c) Nokami T, Matsuo T, Inatomi T, Hojo N, Tsukagoshi T, Yoshizawa H, et-al. Polymer-bound pyrene-4,5,9,10-tetraone for fast-charge and -discharge little stable open-shell molecules.

lithium-ion batteries with high capacity. J Am Chem Soc 2012;134:19694– 700.

[18] (a) Shirota Y, Kinoshita M, Noda T, Okumoto K, Ohara T. A novel class of emitting amorphous molecular materials as bipolar radical formants: 2-[4-[bis(4-methylphenyl)amino]phenyl}-5-(dimesitylboryl)thiophene and 2-[4-[bis(9,9-dimethylfluorenyl)amino]phenyl}-5-(dimesitylboryl)thiophene. J Am Chem Soc 2000;122:11021-2;

(b) Doi H, Kinoshita M, Okumoto K, Shirota Y. A novel class of emitting amorphous molecular materials with bipolar character for electrolumines-cence. Chem Mater 2003;15:1080–9;

(c) Shirota Y, Kageyama H. Charge carrier transporting molecular materials and their applications in devices. Chem Rev 2007;107:953–1010;
(d) Linton KE, Fisher AL, Pearson C, Fox MA, Pálsson LO, Bryce MR, et-al.

J Mater Chem 2012;22:11816–25.

[19] (a) Manecke G, Gauger J. Kondensationsprodukte der quadkatsäure mit primären und sekundären aromatischen aminen. Tetrahedron Lett 1967:3509– 15;

(b) Manecke G, Gauger J. Kondensationsprodukte der quadratsäure mit primären und sekundären aminen. Tetrahedron Lett 1968:1339–43.

- [20] Hünig S, Pütter H. Elektrochemisches Verhalten von Quadratsäure-amiden. Chem Ber 1977;110:2524–31.
- [21] Dirk CW, William CH, Cervantes-Lee F, Selnau H, Martinez S, Kalamegham P, et-al. Squarylium dyes: structural factors pertaining to the negative thirdorder nonlinear optical response. J Am Chem Soc 1995;117:2214–25.
- [22] For examples: (a) Kim SH, Hwang SH. Synthesis and photostability of functional squarylium dyes. Dyes Pigm 1997;35:111–21;
 (b) Ohsedo Y, Miyamoto M, Tanaka A, Watanabe H. Synthesis of new family of squarylium alkylamide and their organogelation ability. New J Chem 2013;37: 2874–80.
- [23] CCDC 932308 (for DPhA-SQD denoted as SQD-1 in CIF file) and CCDC 932309 (for DToIA-SQD denoted as SQD-4 in CIF file) contain the supplementary crystallographic data. It can be obtained free of charge from The Cambridge Crystallographic Data Centre via: www.ccdc.cam.ac.uk/data_request/cif.
- [24] Kennedy AR, Smith WE, Tackley DR, David WIF, Shankland K, Brown B, et-al. Tetraaryl biphenyl diamine hole transport materials: a structural study utilizing both single crystal and high resolution powder diffraction. J Mater Chem 2002;12:168–72.
- [25] Shirota Y. Organic materials for electronic and optoelectronic devices. J Mater Chem 2000;10:1–25.

- [26] Lunelli B, Roversi P, Ortoleva E, Destro R. Geometry and molecular parameters of 3,4-bis(dimethylamino)-3-cyclobutene-1,2-dione and its isomer bis(dimethylamino)squaraine. J Chem Soc Faraday Trans 1996;92:3611–23.
- [27] For estimate the reversibility of electrochemical process, modified Nicholson's equation was used: $I_{pa}/I_{pc} = (I_{pa})_0/I_{pc} + 0.485 (I_{sp})_0/I_{pc} + 0.086$ for one-electron oxidation, see supplementary data for definition of characters and the equitation for two-electron oxidation.
- [28] Bard AJ, Faulkner LR. Electrochemical methods: fundamentals and applications. 2nd ed. John Wiley & Sons, Inc.; 2001 [chapter 6].
- [29] (a) Mkhalid IAI, Bamard JH, Marder TB, Murphy JM, Hartwig JF. C–H activation for the construction of C–B bonds. Chem Rev 2010;110:890–931;
 (b) Surry DS, Buchwald SL. Dialkylbiaryl phosphines in Pd-catalyzed amination: a user's guide. Chem Sci 2011;2:27–50.