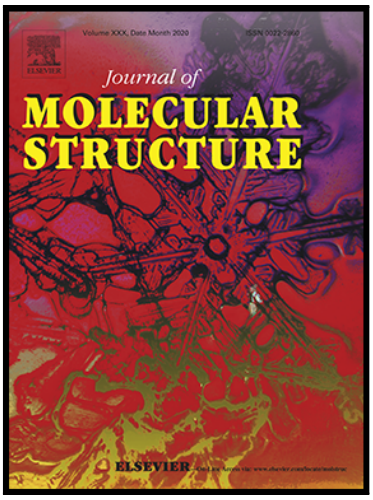

Synthesis, Characterization, DFT and TD-DFT study of Novel bis(5,6-diphenyl-1,2,4-triazines)

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Adel A. Mohamed Software; Validation ,
Maram T.H. Abou Kana Visualization; Investigation ,
Ahmed H.M. Elwahy Conceptualization; Original draft preparation ,
Samy A. El-Daly , El-Zeiny M. Ebeid Reviewing and Editing

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Highlights

- Synthesis of novel series of bis(5,6-diphenyl-1,2,4-triazines).
- Confirmation of their chemical structures by spectroscopic techniques.
- Studies of their absorption and excited-emission spectra experimentally in ethanol solvent.
- Calculation of their electronic absorption and emission spectra in gas and ethanol solvent using time dependent density functional theory (TDDFT).

Synthesis, Characterization, DFT and TD-DFT study of Novel bis(5,6-diphenyl-1,2,4-triazines)

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Abstract: Due to the numerous biological as well as pharmacological activities of 1,2,4-triazine derivatives, we reported a synthesis of novel series of bis(5,6-diphenyl-1,2,4-triazines) *via* alkylation of 5,6-diphenyl-1,2,4-triazine-3(4*H*)-thione with the appropriate bis(halo) compounds in ethanolic KOH. The chemical structures of these compounds were confirmed by spectroscopic techniques. The absorption and excited-emission spectra of the studied novel series were monitored experimentally in ethanol solvent. The molecular structures of these triazines were optimized using B3LYP/6-31G(d) level of theory. The electronic absorption and emission spectra of the novel compounds, in gas and ethanol solvent, were calculated using time dependent density functional theory (TDDFT) at mPW1PW91/ 6-31G (d) level. The obtained theoretical results were compared to experimental ones. The results show that, the computational optical properties of the studied novel series are in agreement with experimental results.

Key words: Bis(5,6-diphenyl-1,2,4-triazines); Optical properties; Fluorescence spectra; Density functional theory (DFT); Time dependent density functional theory (TDDFT).

1. Introduction:

The preparation of novel organic л-conjugated luminophores has been of significant important over the last few decades, because of their wide applications in a lot of fields such as optoelectronics, bio-imaging, and optical storage devices [1-4]. Organic compounds having both electron donating (D) and accepting (A) substituents in a single molecule show great optical and

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spectral properties because of intramolecular charge transfer (ICT). This phenomenon led to substantial manuscripts being of potential applications in photoelectronic and nonlinear optical devices [5], chemical sensing [6], and investigating photochemical and photobiological processes [7]. The photophysical properties of these compounds exhibited very strong solvent polarity dependent [8].

Moreover, 1,2,4-triazine is an important core system and many of their derivatives have gained considerable attention because they are found in numerous natural and synthetic biologically as well as pharmacologically active compounds [9]. 1,2,4-Triazine derivatives have been reported to possess a broad spectrum of biological activities including anti-inflammatory [10] antimicrobial [11, 12], anti-HIV [13], anticancer [14-16], antihaemostatic activity [17], antiviral [18], antimalarial [19], anticonvulsant [16], neuroprotective[20], antifungal [21], antiproliferation [22, 23]. Some 1,2,4-triazine derivatives have also used as kinase inhibitors [24, 25], and α-glucosidase inhibitors [26, 27]. Some drugs containing triazine moiety are outlined in Fig. 1 [28]. The chemistry and biological applications of this class of compounds have been recently reviewed [29].

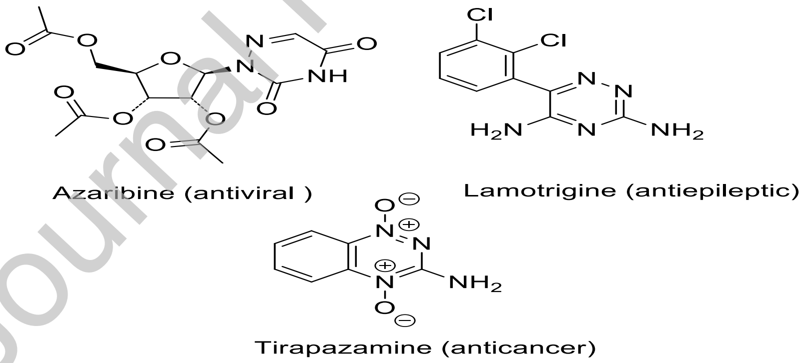


Fig. 1 Some drugs containing triazine moiety**.**

In connection with these findings, we report herein the synthesis of some novel bis(1,2,4-triazines) *via* alkylation of 5,6-diphenyl-1,2,4-triazine-3(4*H*)-thione with the appropriate bis(halo) compounds and to validate the chemical structural model that best describes their electronic properties as well as their chemical reactivity parameters. Density functional theory (DFT) and time dependent density functional theory (TDDFT) were selected to calculate the ground and exited states electronic properties, as well as their electronic spectra which were then compared with the corresponding experimental results.

1. Experimental:

1.1 General

|Infrared spectra were investigated in potassium bromide disks on a PyeUnicam SP3-300 and Shimadzu FTIR 8101 PC infrared spectrophotometer. The ^{1}H NMR spectra were determined on a Varian Mercury VX 300 NMR spectrometer using TMS as an internal standard and DMSO-d6 as a solvent. Mass spectra were recorded on a GCMS-QP1000 EX spectrometer at 70 eV. Elemental analyses were investigated at the Microanalytical Center of Cairo University, Giza, Egypt. All required chemicals were purchased from Sigma Aldrich and used without further purification. The absorption and excited-emission spectra of the novel series of bis(5,6-diphenyl-1,2,4-triazines) were monitored experimentally in ethanol solvent using spectral ultraviolet radiation (Shimadzu UV-2450) and a spectrometer (Shimadzu, RF-5301PC).

1.2 Synthesis of compounds 5, 7 and 9:

To a solution of **3** (10 mmol) and KOH (10 mmol) in absolute ethanol (10 ml) the appropriate dibromo compounds **4**, **6** and **8** (5 mmol) was added. The reaction mixture was heated at reflux for 1 h, allowed to cool to room temperature. The formed crude solid was filtered off, dried and recrystallized from dimethylformamide (DMF) to give yellow crystals of **5, 7** and **9,** respectively.

1,4-Bis((5,6-diphenyl-1,2,4-triazin-3-yl)thio)butane (5)

With the use of the general procedure, compound **3** and 1,4-Dibromobutane **4** gave crude **5** (75%); IR: υ max 3049, 2924 (CH), 1597, 1490 (C=C) cm^{-1}, ^{1}H NMR (DMSO) δ 2.0 (br, 4H, SCH_2CH_2), 3.88 (br, 4H, SCH_2CH_2), 7.32-7.49 (m, 8H, ArHs) ppm. MS: m/z 584 (M^+); Anal. for $C_{38}H_{28}N_6S_2$, Calcd. C, 69.83; H, 4.83; N, 14.37; S, 10.97. Found: C, 70.10; H, 4.60; N, 14.50.

1,4-Bis(((5,6-diphenyl-1,2,4-triazin-3-yl)thio)methyl)benzene (7)

With the use of the general procedure, compound **3** and 1,4-bis(bromomethyl)benzene **6** gave crude **7**, which crystallized from DMF as colorless crystals (84%); IR: υ max 3046, 2930 (CH), 1536, 1487 (C=C) cm^{-1}, ^{1}H NMR (DMSO) δ 4.59 (s, 4H, SCH_2), 7.34-7.48 (m, 24H, ArHs) ppm. MS: m/z 632 (M^+); Anal. for $C_{38}H_{28}N_6S_2$, Calcd. C, 72.13; H, 4.46; N, 13.28. Found: C, 72.40; H, 4.20; N, 13.10.

2,6-Bis(((5,6-diphenyl-1,2,4-triazin-3-yl)thio)methyl)pyridine (9)

With the use of the general procedure, compound **3** and 2,6 bis(bromomethyl)pyridine **8** gave crude **9**, which crystallized from DMF as colorless crystals (85%); IR: υ max 3051, 2938 (CH), 1581, 1493 (C=C) cm^{-1}, ^{1}H NMR (DMSO) δ 4.72 (s, 4H, OCH_2), 7.30-7.74 (m, 23 H, ArH, Pyridine-H) ppm. MS: m/z 633 (M^+); Anal. for $C_{37}H_{27}N_7S_2$, Calcd. C, 70.12; H, 4.29; N, 15.47. Found: C, 70.30; H, 3.90, N, 15.20.

1.3 Computational details

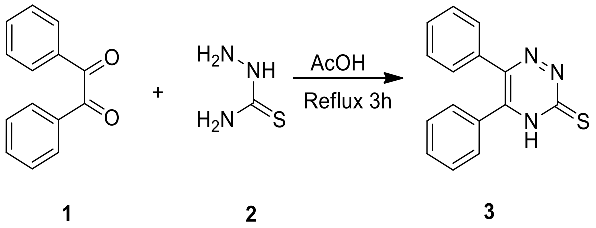
The electronic ground and excited states structures of compounds **3**, 7, **5** and **9** were obtained using the density functional theory (DFT) and the time dependent density functional theory (TDDFT). All calculations were generated with the Gaussian 09 program package [35]. The chemical structure optimizations were carried out at the DFT/6-31G(d) level of theory without any constrains. According to three possible criteria for Pitch gradient drainage, the correlation capabilities were corrected for Lee-Yang-Parr Gradient (B3LYP) [30] and all calculations were generated utilizing the 6-31G (d) basis set.

The electronic absorption and emission spectra of the novel compounds, in gas and ethanol solvent, were calculated using time dependent density functional theory (TDDFT) at mPW1PW91/ 6-31G (d) level.

2. Results and discussions:

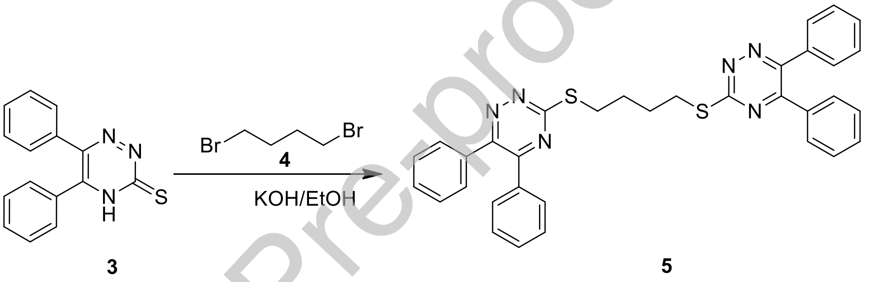
2.1. Synthesis

The starting compound 5,6-diphenyl-1,2,4-triazine-3(4*H*)-thione **3** was synthesized in good yield by heating benzil **1** with thiosemicarbazide **2** in acetic acid at reflux using a previously reported procedure (Scheme 1) [20].



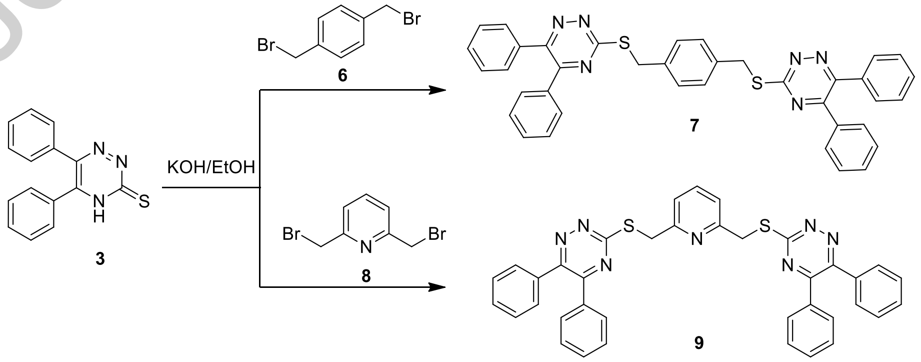
Scheme 1: Synthesis of compound **3**.

The synthetic utility of **3** as building block for novel bis(5,6-diphenyl-1,2,4-triazines) **5, 7** and **9** was investigated as outlined in Schemes 1 and 2. Thus, reaction of **3** with 1,4-dibromobutane **4** in ethanol containing KOH at refluxing temperature afforded 1,4-bis((5,6-diphenyl-1,2,4-triazin-3-yl)thio)butane **5** in 75% yield (Scheme 2).



Scheme 2: Synthesis of compound **5**.

Using a similar approach, the reaction of **3** with 2,6-bis(bromomethyl)benzene **6** in ethanol containing KOH at refluxing temperature afforded 1,4-bis(((5,6-diphenyl-1,2,4-triazin-3-yl)thio)methyl)benzene **(7)** in 84% yield. Similarly, the 2,6-bis(((5,6-diphenyl-1,2,4-triazin-3-yl)thio)methyl)pyridine **(9)** was prepared in 85% yield by the reaction of **3** with 2,6-bis(bromomethyl)pyridine **8** in ethanol containing KOH at refluxing temperature (Scheme 3).



Scheme 3: Synthesis of compounds **7** and **9**.

All the isolated compounds were characterized by elemental analyses, as well as their spectral data which agree with the proposed structures. The structures of bis(5,6-diphenyl-1,2,4-triazines) **5, 7** and **9** were confirmed by IR and, ^{1}H-NMR and mass spectra. Thus, the absence of an absorption band corresponding to NH or C=S stretching frequencies of the parent 5,6-diphenyl-1,2,4-triazine-3(4*H*)-thione **3** in the IR spectrum of **5, 7** and **9** clearly confirmed the formation of bis(5,6-diphenyl-1,2,4-triazine) derivatives. Moreover, the ^{1}H NMR spectra of compound **5** showed two broad signals at δ 2.0 and δ 3.88 each integrated for four protons attributed to the methylene protons of the butyl spacer. The ^{1}H NMR spectra of compounds **7** and **9** showed two singlet signals at δ 4.59 and δ 4.72, respectively, each integrated for four protons characteristic for the OCH_2 protons. All other protons were seen at the expected chemical shifts and integral values. Mass spectra of compounds **5, 7** and **9** showed intense molecular ion peaks at m/z 584, 632 and 633, respectively, in agreement with their respective molecular formulae.

2.2. DFT calculation

The electronic ground state structures of compounds **3**, **7**, **5** and **9** were obtained using the DFT method. The chemical structure optimizations were carried out at the B3LYP /6-31G(d) level of theory and the results are given in Fig. 2. Compound **3** is not planar where one of the two phenyl rings rotates out of the trizine plane by 33.44^o to avoid the steric hindrance.

The C-C bonds connecting the two phenyl rings and the traizine ring have the lengths 1.483 and 1.484 Å, single bond character. This is confirmed on both of HOMO and LUMO MOs, Fig 3. The HOMO MO is localized one (over the traizine and phenyl rings) while the LUMO is delocalized over the target molecule. In case of compounds **5**, **7** and **9,** the nonplanar structure was also found; the phenyl and pyridyl groups rotate with different angles relative to traizine rings (Fig. 3 and Table 1). Consequently, the л-interaction between the different sub-systems in each molecule is small, which will be reflected on their UV-spectra. Both of HOMO and LUOM MOs are localized on certain sub-systems of the target molecule, as shown in Fig. 3. The geometrical parameters of the **3**, **5**, **7** and **9** compounds in gas state are listed in Table 1. The labeling scheme is shown in Fig. 2. Table 1 showed the difference between the bond lengths or angles of the triazine moiety in compound **3** and the other studied molecules.

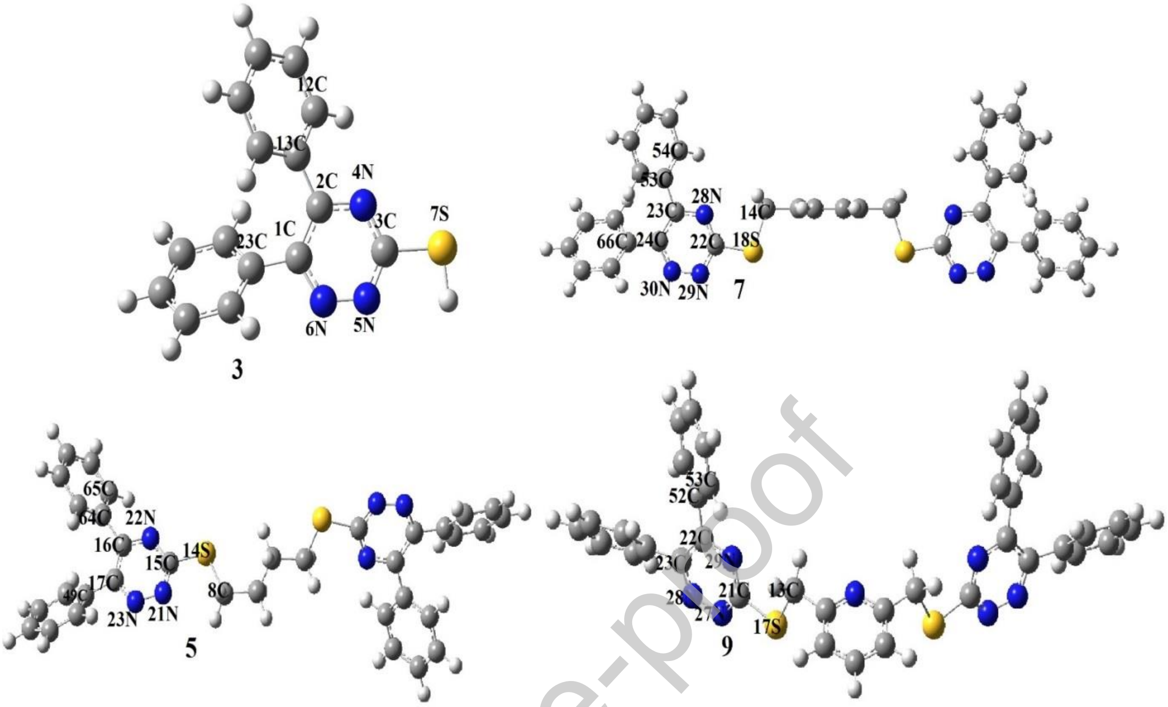


Fig. 2 Optimized geom. of compounds **3, 5, 7** and **9**.

Table 1 Selected optimized geometrical parameters (bond length in Å and dihedral angle in ^{o}) computed for 3, 5, 7 and 9 in gas phase using B3LYP/6-31G(d). For labeling, refer to Fig. 2.

3	parameters	**5**	parameters	**7**	parameters	**9**	parameters
C_2-N_4	1.336	C_{16}-N_{22}	1.332	C_{23}-N_{28}	1.339	C_{22}-N_{29}	1.356
N_4-C_3	1.332	N_{22}-C_{15}	1.337	N_{28}-C_{22}	1.332	N_{29}-C_{21}	1.339
C_3-N_5	1.342	C_{15}-N_{21}	1.340	C_{22}-N_{29}	1.347	C_{21}-N_{27}	1.358
N_5-N_6	1.325	N_{21}-N_{23}	1.328	N_{29}-N_{30}	1.318	N_{27}-N_{28}	1.344
C_1-C_2	1.426	C_{17}-C_{16}	1.429	C_{24}-C_{23}	1.421	C_{23}-C_{22}	1.424
C_2-C_{13}	1.483	C_{16}-C_{64}	1.484	C_{23}-C_{53}	1.484	C_{22}-C_{52}	1.480
C_1-C_{23}	1.484	C_{17}-C_{49}	1.485	C_{24}-C_{66}	1.484	C_{23}-C_{63}	1.480
C_3-S_7	1.772	C_{15}-S_{14}	1.767	C_{22}-S_{18}	1.770	C_{21}-S_{17}	1.816
C_{12}-C_{13}-C_2-N_4	33.44	C_{65}-C_{64}-C_{16}-N_{22}	34.04	C_{54}-C_{53}-C_{23}-N_{28}	148.55	C_{53}-C_{52}-N_{22}-N_{29}	35.49
C_{13}-C_2-C_1-C_{23}	15.04	C_{64}-C_{16}-C_{17}-C_{49}	14.36	C_{53}-C_{23}-C_{24}-C_{66}-	15.13	C_{52}-C_{22}-C_{23}-C_{63}	14.31
		C_{15}-S_{14}-C_{12}-C_7	177.56	C_{22}-S_{18}-C_{14}-C_6	176.67	C_{21}-S_{17}-C_{13}-C_5	179.48
		C_{18}-S_{13}-	176.14	C_{19}-S_{17}-	176.68	C_{18}-S_{16}-	179.49

		C_1-C_5		C_{11}-C_3		C_{10}-C_1	

The graphical presentation of the HOMO-1, HOMO, LUMO, LUMO+1 orbitals, energy gap between HOMO and LUMO (E_{g1}) and between HOMO-1 and LUMO+1 (E_{g2}) for **3**, **7**, **5** and **9** compounds in gas at B3LYB/6-31G(d) level of theory is shown in Fig. 3. It is worth noting that these MOs are mainly localized over certain part of the molecule (traizine and phenyl groups) and not extended over the entire molecule. In addition, the calculated energy values of HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1 and LUMO+2, energy gap between HOMO and LUMO (E_{g1}) and energy gap between HOMO-1, LUMO+1 (E_{g2}) and energy gap between HOMO-2 and LUMO+2(E_{g3}) of the studied compounds are listed in Table 2. The calculated E_{g1} of the studied novel compounds increases in the following order **5** < **9** < **7** < **3** which means that compound **5** has the highest reactivity and compound **3** has lowest reactivity.

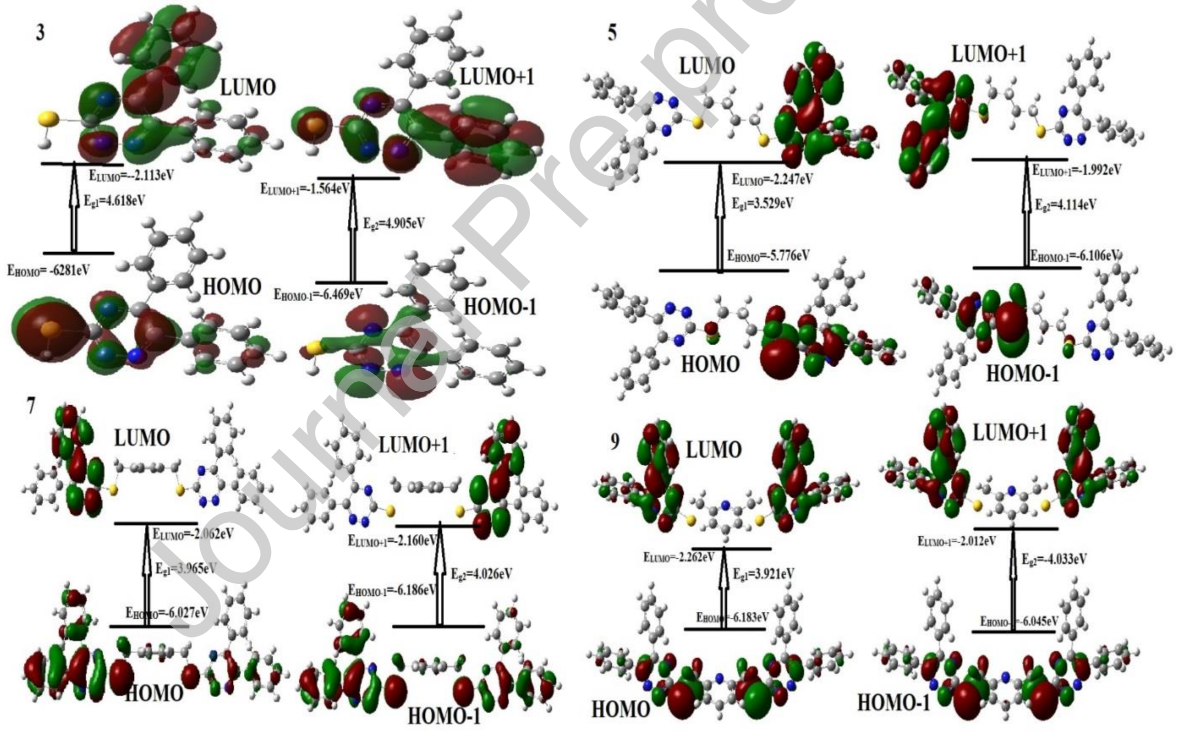


Fig. 3 Graphical presentation of the highest occupied (HOMO), lowest unoccupied molecular (LUMO) orbitals, HOMO-1, LUMO+1 energy gap between HOMO and LUMO (E_{g1}) and energy gap between HOMO-1 and LUMO+1 (E_{g2}) for **3**, **7**, **5** and **9** compounds in gas at B3LYB/6-31G(d) level of theory.

Table 2 Energy values of HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1 and LUMO+2, energy gap between HOMO and LUMO (E_{g1}) and energy gap between HOMO-1, LUMO+1 (E_{g2}) and energy gap between HOMO-2 and LUMO+2(E_{g3}) for **3**, **7**, **5** and **9** compounds in gas at B3LYB/6-31G(d) level of theory.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{g1} (eV)	E_{HOMO-1} (eV)	E_{LUMO+1} (eV)	E_{g2} (eV)	E_{HOMO-2} (eV)	E_{LUMO+2} (eV)	E_{g3} (eV)
3	-6.281	-2.113	4.168	-6.469	-1.564	4.905	-6.920	-0.430	6.490
5	-5.776	-2.247	3.528	-6.106	-1.992	4.114	-6.286	-1.478	4.808
7	-6.027	-2.062	3.965	-6.186	-2.160	4.026	-6.249	-1.626	4.623
9	-6.183	-2.262	3.921	-6.045	-2.012	4.033	-6.300	-1.467	4.833

According to Kobmann theorem the I.P, the ability to lose electron, equal to - E_{HOMO} therefore, the order of I.P values of this series is **5**<**7**<**9**<**3**. On the other hand, E_{LUMO} is related to the electron affinity (E.A), of the compound using the relation E.A = E_{LUMO}. Table 3 shows that order of E.A values of this series is **7** <**3** <**5**< **9;** i.e compound **9** has the highest tendency to accept electrons. The energy gap between frontier molecular orbitals (HOMO and LUMO) is used as a powerful indicator of chemical reactivity, kinetic stability and biological activity of molecular systems. The energy gap (E_g) is given by the difference [E_{LUMO} - E_{HOMO}]. The calculated Eg of the studied 1,2,4-triazine compounds increases in the following order **5** < **9** < **7** < **3** i.e. **5** has higher reactivity. The lowering of Eg value of **5**, **9** and **7** compared to that of **3** indicates less stability, a significant effect of intramolecular charge transfer (ICT), consequently the absorption spectra is red shifted. Another important calculated parameters, using E_{LUMO} and E_{HOMO} values, are the chemical potential (μ), electronegativity (χ) and the chemical hardness (η). These parameter are calculated as follows $\mu = \frac{E_{HOMO} + E_{LUMO}}{2}$ [31], $\chi = -\frac{E_{HOMO}+E_{LUMO}}{2}$ [31] $\eta = \frac{E_{LUMO}-E_{HOMO}}{2}$ [31] and chemical softness (s=1/ η). Generally, when the molecules having a high dipole moment, it has a high asymmetry in the distribution of electronic charge hence, and can be more reactive sensitive to change its electronic molecular structure and its electronic characteristics under an external electric field. As shown in Table 3, the dipole moment (ρ) of the compounds **7** and **9** are higher than that of **3** and **5**. Consequently, these compounds are more reactive. The lower chemical potential value, μ, of compared **9** compared to the other three 1,2,4-triazines (**3**, **7** and **5**) (see Table 3), indicates the tendency of the electrons to escape from compound **9** is lower than that of the others (**3**, **7** and **5**) [31]. Hence, the molecule **9** is considered harder, most stable and least reactive compared to the others [32].

Also, compound **9** has a high χ value than other compounds (**3**, **7** and **9**) (Table 3), thus the molecule **9** is the one that is able to attract the electrons from other compounds. In another side, compound **3** has a high η value in comparison with other three 1,2,4-triazine molecules (**7**, **5** and **9**), this indicates that compound **3** is very difficult to liberate the electrons, while the other 1,2,4-triazine molecules (**7**, **5** and **9**) are good candidates to give electrons to another acceptor molecule (see Table 3).

The excited state life times (τ) of the molecule sensitizers were calculated via utilizing the following formula: ($\tau = 1.499/f\ E^2$) [33], where E is the excitation energy of the different electronic states (cm^{-1}) and *f* is the oscillator strength of the electronic state. The calculated τ values for the four 1,2,4-triazine compounds (3, 7, 5 and 9) are listed in Table 3. Consequently, long radiative lifetimes facilitate the electron transfer via the photoexcited electron, from LUMO of electron-donor to LUMO of electron-acceptor, hence lead to high light-emitting efficiency.

Table 3 Calculated E_{HOMO}, E_{LUMO}, energy gap (E_g), dipole moment (ρ) and other quantum chemical parameters as electronegativity (χ), chemical potential (μ), chemical hardness (η) and excited state life time (τ) values of the studied compounds obtained by B3LYP/6-31G(d) level.

Compounds	*f*	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	μ (eV)	η (eV)	χ (eV)	ρ (D)	τ (ns)
3	0.2400	-6.281	-2.113	4.168	-4.197	2.084	4.197	3.470	5.526
7	0.0057	-6.027	-2.062	3.965	-4.044	1.982	4.044	9.940	0.025
5	0.0028	-5.776	-2.247	3.528	-4.011	1.764	4.011	4.780	0.066
9	0.0057	-6.183	-2.262	3.921	-4.222	1.960	4.222	8.880	0.026

2.3. Electronic absorption and emission spectra

The electronic absorption spectra of the studied compounds were measured experimentally using ethanol as a solvent; the results are given in Fig 4A. The electronic absorption spectrum of 3 in ethanol consists of mainly one peak appearing at 400 nm in the range between 300-600 nm. It is assigned as π-π* transition as indicated by its extinction coefficient, 5280 $Lmol^{-1}cm^{-1}$. Also, Fig. 4A shows that the electronic absorption spectra of 7, 5 and 9 measured in ethanol solvent have the same features. The corresponding λ_{max} and extinction coefficients are (350 nm and 10360 $Lmol^{-1}cm^{-1}$), (350 nm and 9890 $Lmol^{-1}cm^{-1}$) and (350 nm, 11190 $Lmol^{-1}cm^{-1}$), respectively, i.e these bands are blue shifted relative to 3 transition and also assigned as π-π* transitions. This means that less π-conjugation exists over the substituted molecules. On the other hand, the electronic emission spectra of the studied systems were also recorded in ethanol and presented in Fig. 4B. The experimental maximum emission wavelength of the **3** molecule is 446 nm while the experimental maximum emission wavelength of **5, 7** and **9** is 400 nm as shown in Fig. 4B.

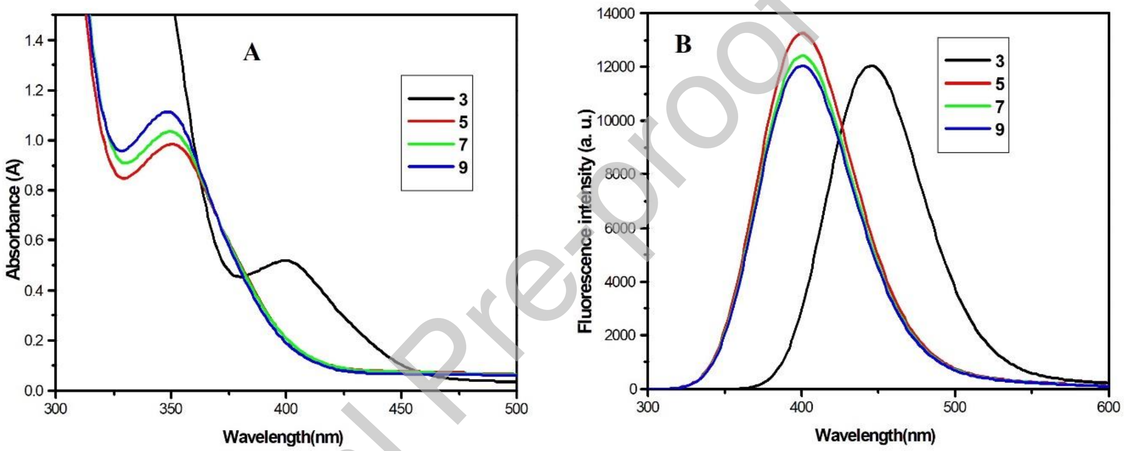


Fig.4 Experimental absorption (A) and emission (B) spectra of compounds 3, 5, 7 and 9 in ethanol (1×10^{-4}M).

To understand the above experimental results, the electronic absorption and emission spectra of the studied systems were calculated in gas and ethanol phases using TDDFT method. To find out the best functional and basis set for calculating electronic absorption spectra of the studied systems, many functionals, B3LYP [30], CAM-B3LYP [34], M06-2X [35], ωB97X-D [36], mPW1PW91 [37, 38], were tested for 7 using 6-31G(d) basis set. The results shown in Fig. 5 indicate that mPW1PW91 gives the nearest results to the experimental data of compound **7**, Table 4. The funstionals CAM-B3LYP, M06-2X, ωB97X-D, underestimates the experimental results while B3LYP overestimates it. The effect of using different basis sets indicates that calculated electronic absorption spectrum of molecule 7 is accurate without diffuse functions. Therefore, involvement of diffuse functions is not essential in obtaining acceptable results.

Hence, the mPW1PW91 functional with the 6-31(d) basis set is used to calculate the optical properties of the all studied molecules.

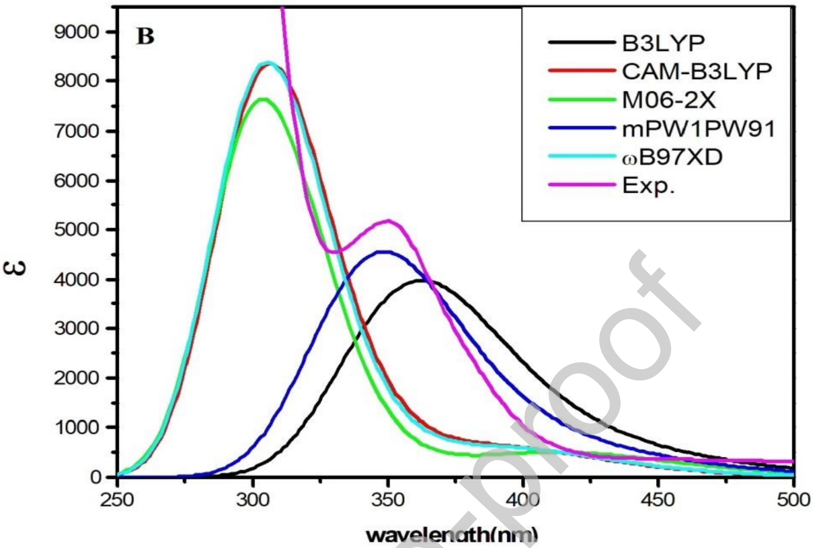


Fig. 5 Calculated absorption spectra of a model compounds **7** obtained with the use of different functionals, B3LYP, CAMB3LYP, M06-2X, ωB97X-D and mPW1PW91 and experimental absorption spectrum of the **7**. Vertical lines in each panel correspond to calculated absorptivity. The 6-31G(d) basis set was applied.

Table 4: Calculated maximum absorption wavelength (Calc. λ_{abs}. (nm)) of a model compound **7** obtained with the use of different functionals, B3LYP, CAMB3LYP, M06-2X, ωB97X-D and mPW1PW91 and experimental absorption wavelength (Exp. λ_{abs}. (nm)). The 6-31G(d) basis set was applied.

Molecular compounds	Dependence of the DFT functionals	Calc. λ_{abs}. (nm)	Exp. λ_{abs}. (nm)
7	B3LYP	363	350
	CAMB3LYP	306	
	M06-2X	303	
	mPW1PW91	349	
	ωB97X-D	305	

The calculated electronic absorption and emission spectra of the **3, 7, 5** and **9** molecules, in gas and ethanol, are generated via utilizing mPW1PW91/ 6-31G (d) level as shown in (Figs. 6) and the corresponding parameters are given in Table 5. The calculated electronic absorption spectrum of **3** in gas phase appears as three transitions at 390, 332 and 382 nm while in ethanol at 379, 337 and 291 nm, Table 5, due to the variation of the stabilization of ground and excited states in polar solvent. The first one corresponding to the experimental peak at 400 nm (f = 0.005) predominately arises from transition of MO68 -> 70. On the other hand, second band (f = 0.110) arises from transition of MO69 -> 70 and the third one f = 0.1210. On substitution of **3**, the calculated electronic absorption spectra of the **7**, **5** and **9** molecules in both phases recorded via utilizing the same level are given Fig 6 and Table 5. The three calculated transitions for **5** appear at 416nm (f = 0.007), 348 nm (f = 0.048) and 335 nm (f = 0.001) in gas. The second one corresponds to the experimental one (350 nm) and arises from the transition MO153 ->155 and it does not affect by solvent. The same findings were also found for both **7** and **9** but with red shift for the experimentally calculated one.

The calculated maximum emission wavelength of molecule **3** is 365 nm, while the experimental maximum emission wavelength is 446 nm in ethanol as shown in Fig. 6A. The calculated maximum emission wavelength of **7**, **9** and **5** are 415, 410 and 430 nm, respectively, in ethanol whereas the experimental wavelengths are 400 nm as shown in Fig. 6B, 6C and 6D.

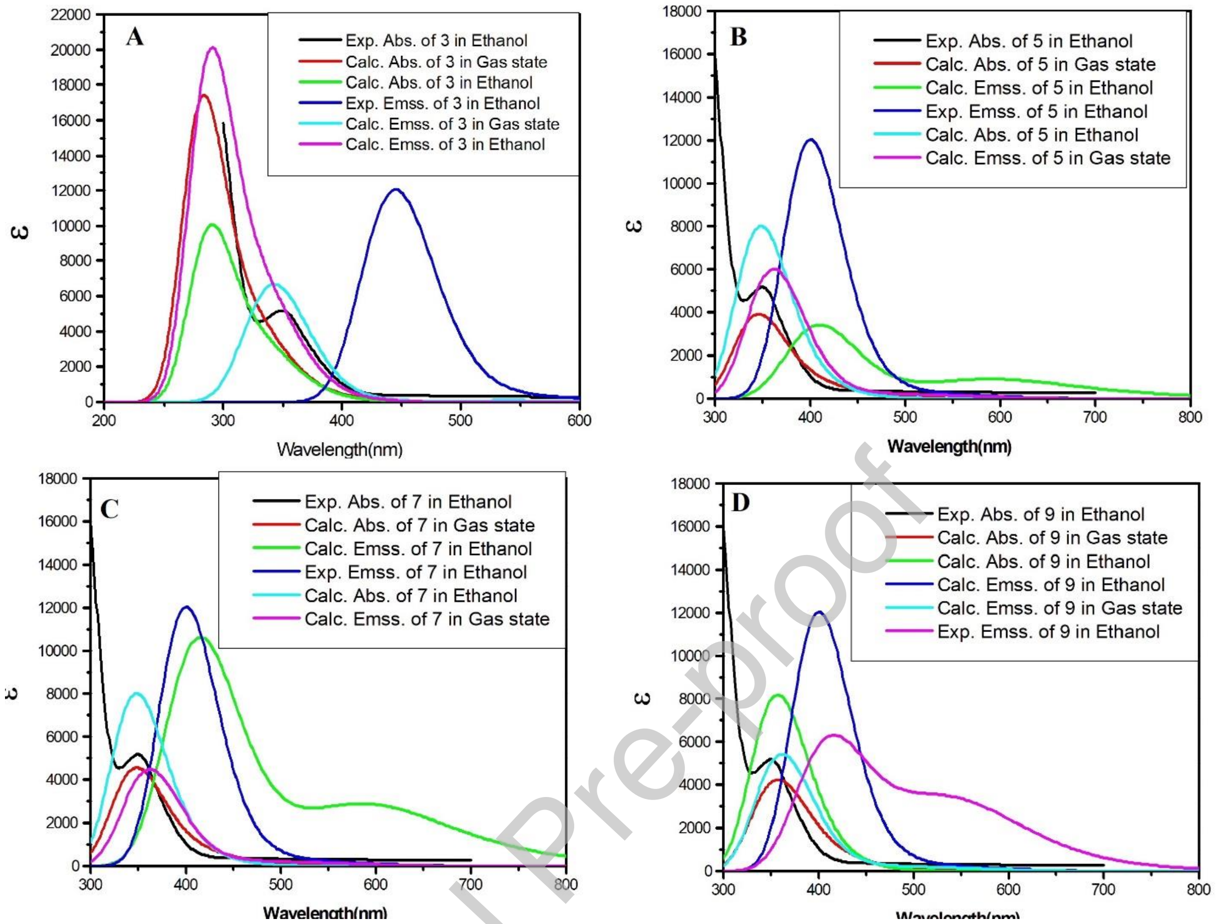


Fig. 6 Calculated electronic absorption (Calc. Abs.) and emission spectra (Calc. Ems.) of compounds **3** (A), **5** (B), **7** (C) and **9** (D) obtained and the experimental absorption (Exp. Abs.) and emission spectra (Exp. Ems.) of the **3** (A), **5** (B), **7** (C) and **9** (D). Vertical lines in each panel correspond to calculated absorptivity. The mPW1PW91 functional was applied with 6-31G (d) basis set.

Table 5 Calculated electronic absorption parameters for compounds 3, 5, 7 and 9. The mPW1PW91 functional was applied with 6-31G (d) basis set.

Compound	Solvent	Excited state	Electronic transition	ΔE (eV)	f	Coefficient	Exp. $\lambda_{abs.}$ (nm)
3	Gas	1	68 -> 70 68 -> 71	3.1808 (390 nm)	0.005	0.936 0.036	400
		2	68 -> 71 69 -> 70	3.7305 (332 nm)	0.110	0.048 0.918	
		5	66 -> 70 67 -> 70 69 -> 71	4.3883(282 nm)	0.1210	0.190 0.540 0.220	
	Ethanol	1	64 -> 70 68 -> 70 68 -> 71	3.272(379 nm)	0.005	0.0002 0.9230 0.0233	
		2	69 -> 70	3.673(337 nm)	0.1259	0.959	
		5	66 -> 70 67 -> 70 69 -> 71	4.265(291 nm)	0.1925	0.231 0.392 0.343	
5	Gas	1	151 ->155 151 ->157	2.976(416 nm)	0.0063	0.930 0.053	350
		3	151 ->155 151 ->157 153 ->155	3.563(348 nm)	0.0476	0.027 0.041 0.891	
		6	150 ->156 150 ->164 152 ->154 152 ->156	3.699(335 nm)	0.0018	0.806 0.021 0.061 0.075	
	Ethanol	1	151 ->154 151 ->155	3.124(397 nm)	0.007	0.877 0.068	
		3	153 ->154 153 ->155	3.564(348 nm)	0.088	0.884 0.078	
		5	151 ->156	3.833(323 nm)	0.079	0.870	
7	Gas	1	162 ->166 163 ->167	2.973(417 nm)	0.0025	0.462 0.460	350
		3	162 ->169 163 ->168 164 ->167 165 ->166	3.557(348 nm)	0.0187	0.021 0.021 0.422 0.468	
		5	162 ->169 163 ->168 164 ->167 165 ->166	3.638(341 nm)	0.0014	0.408 0.421 0.027 0.030	
	Ethanol	1	161 ->167 162 ->166 163 ->167	3.123 (397 nm)	0.002	0.022 0.474 0.449	
		3	164 ->167 165 ->166	3.564 (348 nm)	0.049	0.461 0.499	
		5	162 ->169 163 ->168	3.828(324 nm)	0.001	0.428 0.419	
9	Gas	1	162 ->167	2.968(418 nm)	0.001	0.460	350

			163 ->166			0.465	
		3	164 ->167 165 ->166	3.475(357 nm)	0.0024	0.447 0.484	
		5	162 ->168 162 ->169 163 ->168 163 ->169	3.684(336 nm)	0.0004	0.331 0.126 0.138 0.276	
	Ethanol	1	162 ->167 163 ->166	3.105(399 nm)	0.001	0.466 0.460	
		3	164 ->167 165 ->166	3.480(356 nm)	0.011	0.468 0.495	
		5	162 ->168 162 ->169 163 ->168 163 ->169	3.865(320 nm)	0.001	0.384 0.041 0.052 0.361	

Conclusion: with the appropriate bis(bromo) compounds in ethanolic KOH.

We synthesized a novel series of bis(5,6-diphenyl-1,2,4-triazines) by alkylation of 5,6-diphenyl-1,2,4-triazine-3(4*H*)-thione with the appropriate bis(bromo) compound in ethanolic KOH. The chemical structures of these compounds were confirmed using spectroscopic data as well as elemental analyses. The mPW1PW91 functional with the 6-31G (d) basis set is used to calculate the ground state and optical properties of the novel triazine molecules 3, 5, 7 and 9. The optimized chemical structures of the studied compounds were found to be not planar where one of the two phenyl rings rotates out of the trizine plane to avoid the steric hindrance. The π-interaction between the different sub-systems in each molecule is small, which reflected on their UV-spectra. Utilizing HOMO and LUMO energy values for triazine molecules, the IP, EA, the energy gap (E_g), chemical potential (μ), electronegativity (χ), chemical hardness (η), dipole moment (ρ) and excited state life time (τ) parameters were successfully investigated and compared. The measured electronic absorption spectrum of 3 in ethanol consists of one π-π^* transition at 400 nm while the corresponding λ_{max} of 7, 5 and 9 is blue shifted relative to that of 3 due to less π-conjugation over the substituted molecules (350 nm). This means that less π-conjugation exists over the substituted molecule. The calculated electronic absorption spectrum of **3** in gas phase appears as three transitions at 390, 332 and 382 nm while in ethanol at 379, 337 and 291 nm, due to the variation of the stabilization of ground and excited states in polar solvent. The maximum emission wavelength of **3** is 446 nm while that of **5**, **7** and **9** is 400 nm.

Conflict of Interest

The authors declare that they have no conflict of interest.

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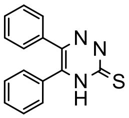
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical Abstract



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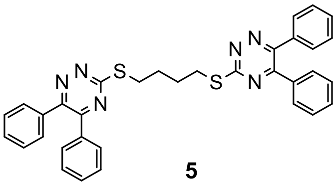

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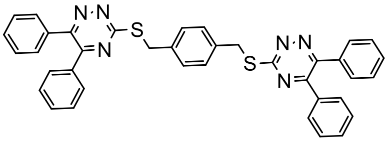

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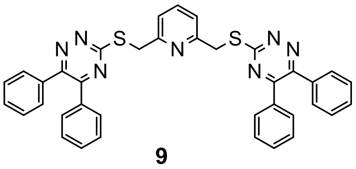

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