ACS Sustainable Chemistry & Engineering

Research Article

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Solvent-Free Microwave-Assisted Synthesis of 2,5-Dimethoxyphenylaminotriazines

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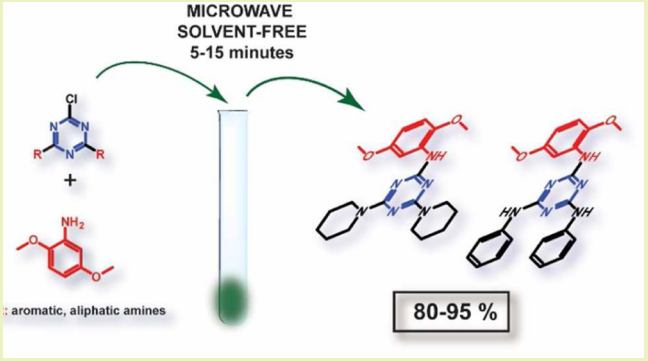
Supporting Information

ABSTRACT: The green synthesis of asymmetric star-shaped 2,5-dimethoxyphenylamino-1,3,5-triazine derivatives using microwave irradiation in the absence of solvent is described. The title compounds have been characterized, and their properties as donor−acceptor (D−A) systems have been studied by UV−vis, fluorescence spectroscopy and electrochemical studies. The formation of excimers and the aggregation of these star-shaped triazine systems have been demonstrated.



KEYWORDS: *Green chemistry, Microwave, Solvent-free, 1,3,5-Triazine, Donor−acceptor systems*

INTRODUCTION

The use of enabling and green technologies to improve the preparation of valuable substances remains a challenge. The main issues in contemporary organic synthesis concern improvements in the efficiency, milder conditions, selectivity, and the avoidance of toxic reagents and the formation of byproducts. From this point of view, the development of new 1,3,5-triazine derivatives in materials and supramolecular chemistry has recently gained importance. The *s*-triazine ring has shown excellent potential for the formation of noncovalent bonds,[1] which involve the nitrogen lone-pairs (coordination and H-bonds), the σ backbone (anionic−σ and electron rich−σ interactions), and/or the heteroaromatic π-electrons (π−π stacking).

Melamine derivatives have important applications in several fields, such as medicinal chemistry,[2] catalysis,[3] the synthesis of polymers,[4] or as components of host−guest,[5,6] and superstructure assemblies.[7] In materials chemistry, 1,3,5-triazine derivatives have been used as acceptors (A) in star-shaped systems. Attractive examples of A-π-D structures that contain the *s*-triazine core include tetrathiafulvalene,[8] thiophene,[9] ferrocene,[10] 1,2,3-triazole,[11] styrylbenzene,[12] 2-pyridyl,[13] and bisphenylaminobenzene[14] units as donors (D). A careful choice of the donor substituents allows the optoelectronic properties to be tuned, thus making these materials suitable for use in luminescent liquid crystals,[11,15] redox active chromophores,[8] photovoltaic devices,[9,14,16] two photon absorption (TPA) materials,[17] and blue phosphorescent OLEDs.[18]

We describe here the preparation of new star-shaped derivatives of *s*-aminotriazines with 2,5-dimethoxyaniline as the donor system, using the green methodologies described by our group, i.e., microwave irradiation and solvent-free conditions.

RESULTS AND DISCUSSION

Synthesis of Triazines 3a−e. The most important method for the synthesis of aminotriazines is the nucleophilic displacement of chloro-substituents from cyanuric chloride. The substitution of these chloro-substituents can be controlled by the reaction temperature, and they can be replaced in a stepwise manner. In general, monosubstitution occurs below or at 0 °C and disubstitution at room temperature, whereas trisubstitution requires high temperatures and long reaction times,[19,20] and may give low yields.[21] Conditions for the third substitution depend on the strength of the nucleophile, the steric characteristics of the substituents in the nucleophile and the triazine ring, and the nature of the solvent. Microwave irradiation has proven to have a very positive effect on the third substitution reaction as yields can be improved and reaction

Received: September 22, 2015
Revised: November 2, 2015
Published: November 8, 2015

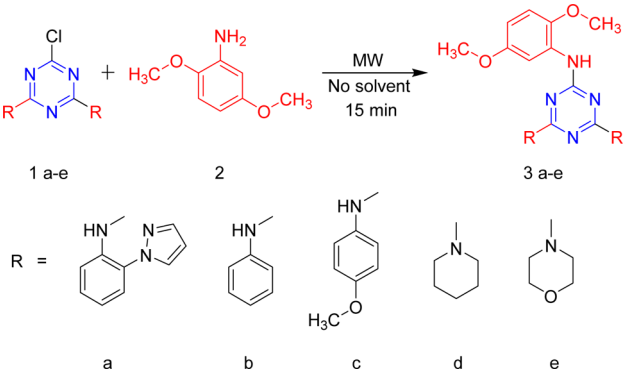
DOI: 10.1021/acssuschemeng.5b01136
ACS Sustainable Chem. Eng. 2015, 3, 3405−3411

times shortened. For instance, we previously described the preparation of trisubstituted 1,3,5-triazines from 2-chloro-4,6-disubstituted triazines in high yield using microwave irradiation as the heating method.[22]

The introduction of an amino group requires ammonia and temperatures of 100−105 °C for 8 h in a closed vessel or the preparation of 2,4-dichloro-6-aminotriazine and reaction with amines at high temperatures.[23] Under such harsh conditions, microwave irradiation has proven to be very efficient for the reduction of reaction times, and as a consequence, decomposition of reagents and products is avoided, isolation procedures are simplified, and yields are higher.[24]

The new star-shaped triazine derivatives were obtained by using 2,5-dimethoxyaniline (**2**) as the nucleophile. The methoxyl groups enhance the donor character of the system, and this modifies both the optical and the binding properties. The target compounds **3a−e** were synthesized as shown in Scheme 1.

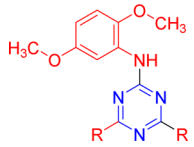
Scheme 1. Green Synthesis of Star-Shaped Triazines 3a−e

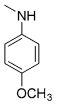


The reaction conditions were optimized with the disubstituted triazine **1a**, which was previously prepared by our group[25] (Table 1). 2,5-Dimethoxyaniline (**2**) was used in 2-fold excess as it was used as a nucleophile, a hydrochloride acceptor, and as the liquid phase to homogenize the reaction mixture.[26] Reactions were optimized with times of 5−15 min and temperatures from 100 to 150 °C using a monomode microwave reactor. The best results were obtained in the absence of solvent, and 90% yield was obtained in only 15 min at 150 °C (entry 1 vs 3, Table 1). The results obtained on extending the method to other amines as nucleophiles are gathered in Table 1 (entries 4−7), and it was found that microwave irradiation is the best methodology to carry out successfully the third substitution reaction in terms of yield, mildness of the conditions, and sustainability. The presence of numerous hydrogen bond donors and acceptors means that these compounds exhibit very promising binding properties.

NMR Spectroscopy. All compounds were characterized by NMR spectroscopy (^{1}H, ^{13}C, gHSQC, and COSY). At 25 °C, the ^{1}H NMR spectra of the title compounds showed broad signals, a finding that has been explained as being due to a restricted rotation of the amino−triazine bond. This process was previously studied by our group and others.[22,27−29] At 80 °C, rotation is a rapid process, and signals consistent with a single compound were observed (Figures S1 and S1a in the Supporting Information). For this reason, the NMR spectra were recorded at 80 °C in solutions in DMSO.

Table 1. Synthesis of Triazines 3a−e under Solvent-Free Conditions



Entry[a]	R	t (min)	Yield (%)[b]
1		5	80
2		10	85
3	**3a**	15	90
4		15	95
	3b		
5		15	90
	3c		
6		15	85
	3d		
7		15	80
	3e		

[a]150 °C, 200 W. [b]Isolated yields.

Optical Properties. The normalized UV and PL spectra of triazines **3a−e** were recorded in dichloromethane at room temperature (Figure 1 and Table 2). The maximum absorption wavelengths are located in the UV region, at around 300 nm, and are attributed to $\pi-\pi^*$ transitions due to the high extinction coefficients.[11]

Two absorption bands at around 259 and 305 nm were observed for triazines **3d** and **3e**, which contain aliphatic amines, while a band at 271−277 nm and a shoulder at 305 nm were observed for **3a−c**, which contain aromatic amines as

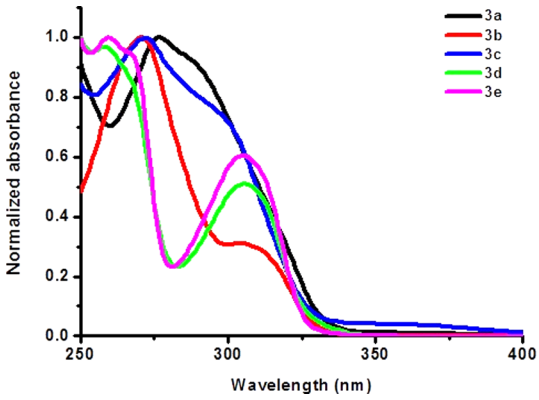


Figure 1. Normalized absorption spectra of triazines in CH_2Cl_2 [10^{-5} M], **3a** (*o*-PyrazolylC$_6$H$_4$, black line), **3b** (PhNH, red line), **3c** (*p*-CH$_3$OC$_6$H$_4$NH, blue line), **3d** (piperidino, green line), and **3e** (morpholino, magenta line).

DOI: 10.1021/acssuschemeng.5b01136
ACS Sustainable Chem. Eng. 2015, 3, 3405−3411

Table 2. Spectroscopic Data for Triazines 3a−e in CH_2Cl_2 [10^{-5} M]

entry	prod	λ_{abs} (nm) [log ε]	$\lambda_{fluoresc}$ (nm)	λ_{excit} (nm)	Stokes shift (cm^{-1})	Φ_F
1	**3a**	277 [4.90]	340	283	6602	0.0011
			398	283, 337		
2	**3b**	271 [4.16]	343	284	7745	0.0007
		305 [4.35]				
3	**3c**	272 [4.43]	330	280	6461	0.005
4	**3d**	259 [4.54]	340	270, 306	3375	0.003
		305 [4.27]	405	283, 339		
5	**3e**	259 [4.59]	340	271, 304	3375	0.0012
		305 [4.37]	396 (sh)			

substituents. A red shift was observed in the absorption spectra of aromatic derivatives **3a**, **3b**, and **3c** ($\lambda \approx 270$ nm) in comparison to aliphatic compounds **3d** and **3e** ($\lambda = 259$ nm), and this is consistent with the higher level of conjugation in aromatic triazine derivatives.[30] The more marked bathochromic shift in **3a** ($\lambda = 277$ nm) can be attributed to the presence of an intramolecular hydrogen bond between the pyrazole nitrogen and the aminotriazine, which increases the planarity of the system and therefore the conjugation. It is clear that the optical properties can be tuned by the donor substituent attached to the triazine ring. The Stokes shifts are higher for the aromatic derivatives, but they are not high enough to show the presence of charge transfer bands.

The emission spectra of triazines **3** showed emission bands with maxima at around 340 nm. Moreover, a band or an intense shoulder was also observed at around 400 nm due to the presence of excimers in solution (Figure 2 and Table 1). The

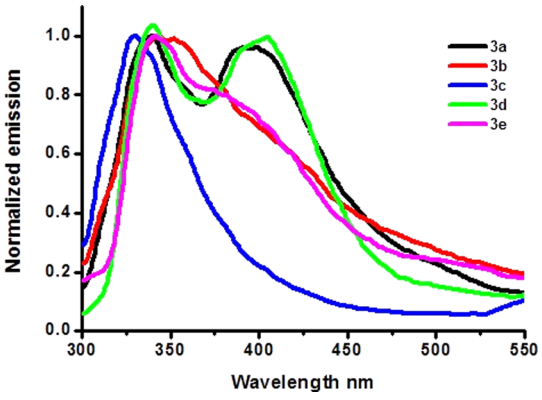


Figure 2. Normalized PL spectra of triazines in CH_2Cl_2 [10^{-5} M]. **3a** (*o*-PyrazolylC$_6$H$_4$, black line), **3b** (PhNH, red line), **3c** (*p*-CH$_3$OC$_6$H$_4$NH, blue line), **3d** (piperidino, green line), and **3e** (morpholino, magenta line).

emission wavelengths in excimers appear at higher wavelengths than the emission in the excited monomers. The formation of excimers was confirmed by recording the PL spectra at different concentrations in CH_2Cl_2 (Figures 3 and S3e).[31] At lower concentrations, intense bands above 340 nm (emission of the excited monomer) and a shoulder at ca. 400 nm were observed. At higher concentration (10^{-3} M), the situation was reversed, with the spectrum containing an intense band close to 400 nm (emission of the excimers) and a shoulder at 340 nm, which is

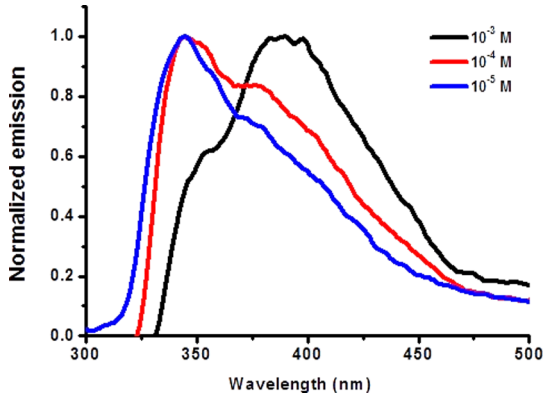


Figure 3. Normalized PL spectra of triazine **3e** in CH_2Cl_2 at different concentrations. 10^{-3} M (black line), 10^{-4} M (red line), and 10^{-5} M (blue line).

consistent with the existence of associations in the excited state. The low photoluminescence quantum yield (PLQY) values obtained for theses derivatives can be explained by the low-lying $n \rightarrow \pi^*$ transitions, which favor intersystem crossing processes.[32,33]

The emission spectra of triazine **3a** in different solvents (hexane, CH_2Cl_2, and MeOH) are given in Table 3 and Figure

Table 3. Emission Maxima of Triazine 3a in Different Solvents

solvent	hexane	DCM	MeOH
λ (nm)	348	339	398

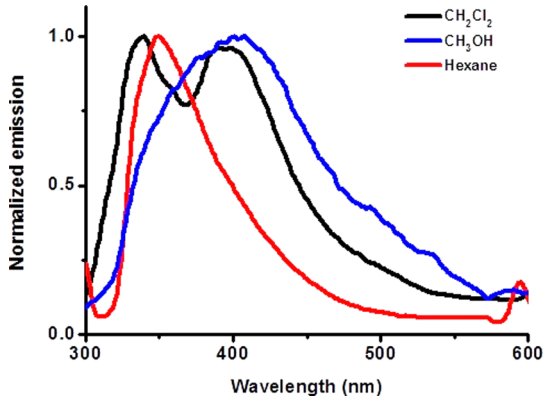


Figure 4. Normalized fluorescence spectra of **3a** in hexane (red line), dichloromethane (black line), and methanol (blue line).

4. A study of the solvatochromism was inconclusive. First, the bathochromic shift found in MeOH can be explained by the ability of this solvent to form hydrogen bonds, a situation that favors charge separation and reduces the energy gap between fundamental and excited states. However, formation of excimers is clear in CH_2Cl_2, which is a solvent that promotes aggregation of the triazines.[34]

Aggregation Studies. The absorption spectra and excitation spectra at 400 nm of triazines **3a** and **3d** (entries 1 and 4, Table 2) (Figures S1d and S4d) are not superimposable, and as a consequence, it can be assumed that aggregates are formed in solution.[33] Consequently, self-assembly assays were

DOI: 10.1021/acssuschemeng.5b01136
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carried out on the synthesized triazines by dynamic light scattering (DLS) in CH_2Cl_2 (Figures 5, S2e, S4e, and S5e). The

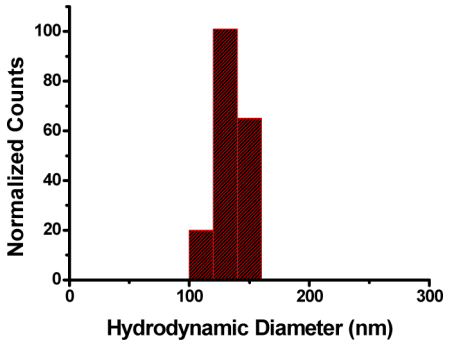

Figure 5. Dynamic light scattering (DLS) of **3a** in CH_2Cl_2 (10^{-2} M). Hydrodynamic diameter = 130 nm.

hydrodynamic diameters of these 2,4-dimethoxyphenylamino-1,3,5-triazines **3** were in the range from 43 nm for **3d** (R = piperidine) to 296 nm for **3b** (R = Ph) (Table 4), and this showed the influence of different substituents connected to the triazine ring.

Table 4. Hydrodynamic Diameters of Triazines 3 in CH_2Cl_2 (10^{-2} M)

product	3a	3b	3d	3e
hydrodynamic diameter (nm)	130	296	43	171

Electrochemical Properties. The relative donor and acceptor behavior of triazines **3a–e** was compared by carrying out electrochemical measurements. The redox potentials of the molecules were measured by Osteryoung square wave voltammetry (OSWV) and by cyclic voltammetry (CV). All of the measurements were performed in DMSO containing tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte. Ferrocene was used as an external reference. Redox data for all of the compounds are collected in Table 5.

Table 5. Redox Potentials (V vs the Ferrocene/Ferrocenium Couple Fc/Fc^+) of the Processes Observed by OSWV[a]

prod	E^2_{red}	E^1_{red}	E^1_{ox}	E^2_{ox}	E^3_{ox}
3a	−3.85	−3.23	0.66	0.87	1.14
3b	−3.32	−3.02	0.61	0.99	
3c	−3.41	−3.06	0.70[b]		
3d	−3.27	−2.96	0.65		
3e	−3.29	−2.99	0.58		

[a]Measured on 2×10^{-3} M solutions in DMSO; the $Ag/AgNO_3$ (0.01 M) electrode was used as a reference and checked against the Fc/Fc^+ couple; glassy carbon electrode; Pt counter electrode; 20 °C, 0.1 M Bu_4NPF_6, and scan rate = 100 mVs^{-1}. [b]Process corresponding to the overlap of two peaks.

In the anodic window, the contribution of each donor substituent can be observed. The OSWV traces for molecules **3a–e** are depicted in Figure 6. The value and the number of oxidation potentials are influenced by the electron richness. In all of the compounds, the first oxidation potentials, at approximately 0.6–0.7 V, are nonreversible and are attributed

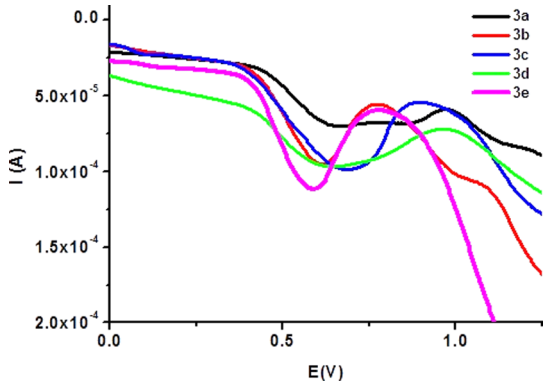

Figure 6. OSWVs for molecules **3a–e** in DMSO containing 0.1 M Bu_4NPF_6. **3a** (black line), **3b** (red line), **3c** (blue line), **3d** (grean line), and **3e** (magenta line).

to the 2,5-dimethoxyphenyl group. For molecules **3d–e**, this is the only active species in the anodic window. The only difference is that the value is slightly lower in **3d**. Further oxidations were observed in molecules **3a–c**, which contain additional aromatic donor substituents. An additional oxidation process was evident for molecules **3b** and **3c**, where the aromatic donor is not fully conjugated with the triazine core. In these systems, the oxidation potentials of the substituent are consistent with the donor strength. The lower electron donor group (phenyl) is oxidized at 0.99 V, and the higher (*p*-methoxy) is oxidized at 0.7 V together with the 2,5-dimethoxyphenyl group. Two further oxidation peaks were observed for triazine **3a**. This compound has the largest planar structure and has two extra oxidation potentials, one for each of the *o*-pyrazolylphenyl groups. The oxidation of the first substituent influences the oxidation potential of the second. This situation is consistent with the existence of electronic communication through the triazine bridge. Molecule **3a** is therefore an example of a mixed valence system in its oxidized state.[35]

In the cathodic region, the reduction processes are attributed to the triazine core. The lowest reduction potentials were observed for compound **3a**, in which triazine is more electron rich due to the extended conjugation. In compounds **3b–c**, the acceptor ability of the triazine is preserved by the interruption of the conjugation with the substituents. The reduction potentials of the molecules with a large aromatic structure (**3b–c**) are barely higher than that in the molecules with aliphatic substituents (**3c–d**).

The electrochemical measurements indicate a clear correlation between the electron-richness and the acceptor ability of the triazine. The results show that a lack of conjugation has a low impact on the reduction potentials. The conjugation of donor substituents leads to a decrease of 200 mV in the reduction potentials. In addition, the conjugation of several donors with the triazine core leads to the formation of a large conjugated structure in which the triazine behaves as a bridge.

CONCLUSIONS

A new series of asymmetric star-shaped 1,3,5-triazines has been synthesized using a sustainable, rapid, clean, and selective method based on the use of microwave irradiation and solvent-free conditions.

The UV–vis and photoluminescence (PL) spectra as well as DLS studies showed the aggregation in the ground and excited

DOI: 10.1021/acssuschemeng.5b01136
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states. The electrochemical and optoelectronic properties can be tuned by altering the substituent linked to the triazine core.

These new star-shaped triazines can be described as donor (substitutent)−acceptor (triazine) systems that can be easily modulated with the electronic character of the substituent attached to the triazine moiety.

EXPERIMENTAL SECTION

General. All reagents and solvents were commercially available and were used without further purification. Thin layer chromatography was performed on Merck F254 silica gel plates. Flash chromatography was performed on Merck type 60 silica gel (230−400 mesh). Reactions under microwave irradiation were performed in a CEM Discover microwave reactor. Reaction temperatures were measured with an IR pyrometer. Melting points were determined on a Büchi M-565 apparatus without correction. IR spectra were recorded on a Shimadzu IR PRESTIGE-21 spectrophotometer.

NMR spectra were recorded on a Varian Inova-500 spectrometer working at 499.772 MHz for ^{1}H and 125.423 MHz for ^{13}C NMR, the internal standard was the signal of the deuterated solvent; δ in ppm; coupling constants (J) in Hz. Mass spectra were obtained by ESI$^+$ on a QSTAR pulsar i from Applied Biosystems, using formic acid (0.1%) in methanol as the ionizing phase and applying an external calibration to obtain the exact mass.

DLS experiments were performed with a scattering angle of 90° and a 635 nm, 35 mW diode laser source to determine the hydrodynamic diameters. The corresponding solutions (3 mL) were placed in a 1 cm path length cuvette. Each sample was run 10 times, and each run lasted 5 min at 298 K. The data were fitted using the non-negatively constrained least-squares (NNLS) algorithm to solve the experimentally measured autocorrelation function.

UV−vis spectra were recorded on a Jasco V-530 spectrophotometer, and fluorescence spectra were recorded on a Jasco FP-750 spectrofluorimeter using standard quartz cuvettes (1 cm width). In both cases, spectra were recorded at ambient temperature using spectroscopic grade dichloromethane. Solutions were prepared by dilution of a 10^{-3} M stock solution of the products.

Quantum yields were determined experimentally using as standard a solution of anthracene in EtOH (Φ_F = 0.27) and applying the following equation:[36]

$$\Phi_{Fsa} = \Phi_{Fst} \times (A_{st}/A_{sa}) \times (I_{sa}/I_{st}) \times (n_{sa}/n_{st})^2$$

where sa = sample; st = standard (anthracene in EtOH); A = absorbance; I = integration of corrected fluorescence spectrum; and n = refractive index of the solvent.

Reduction (E_{red}) and oxidation (E_{ox}) potentials were measured by cyclic voltammetry and OSWV with an μAutolab II potentiostat in a conventional three-electrode cell equipped with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/$AgNO_3$ reference electrode at a scan rate of 100 mVs^{-1}. The E_{red} and E_{ox} values are expressed versus Fc/Fc^+ as an external reference. In each case, the measurements were carried out in a deaerated solution containing 2 mM of a the sample compound in 0.1 M $(n\text{Bu})_4\text{NPF}_6$ in dry DMSO as an electrolyte solution.

General Preparation of Triazine Derivatives ***3***. In a microwave flask, the appropriate chlorotriazine[25] (**1**) (0.25 mmol) and 2,5-dimethoxyaniline (**2**) (0.078 g, 0.50 mmol) in a 1:2 ratio were introduced and homogenized. The mixture was submitted to microwave irradiation at ambient pressure for 15 min at 200 W (150 °C) without the solvent. The crude product was cooled, washed with CH_2Cl_2 (5 mL), and filtered through a column on silica gel (10 mm high × 12 mm wide) using ethyl acetate as eluent. The mixture was washed first with 1 or 0.1 M HCl (5 mL) (*vide infra*) and then with a saturated solution of sodium carbonate (5 mL). The pure product was filtered off under reduced pressure.

N^2-(2,5-Dimethoxyphenyl)-N^4,N^6-bis(2-(1H-pyrazol-1-yl)phenyl)-1,3,5-triazine-2,4,6-triamine ***3a***. The title compound was synthesized from N^2,N^4-bis(2-(1*H*-pyrazol-1-yl)phenyl)-6-chloro-1,3,5-triazine-2,4-diamine (**1a**) (0.110 g, 0.25 mmol) and 2,5-dimethoxyaniline (**2**) (0.078 g, 0.50 mmol) in a 1:2 ratio, following the general procedure and washing the mixture with 1 M HCl. Filtration under vacuum afforded pure **3a** as a white solid (0.126 g, 90%). mp 178−180 °C (decomp.). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 3.67 (s, 3H), 3.79 (s, 3H), 6.53 (d, J = 1.8 Hz, 2H,), 6.59 (dd, J = 8.8, 2.9 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 2.6 Hz, 1H), 7.81 (d, J = 1.1 Hz, 2H), 7.87 (s, 1H), 8.15 (d, J = 2.6 Hz, 2H), 8.19 (d, J = 8.1 Hz, 2H), 9.44 (s, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 56.30, 57.21, 106.65, 107.83, 108.33, 111.71, 123.53, 123.55, 124.28, 127.07, 128.18, 130.66, 130.79, 131.44, 140.47, 143.54, 152.99, 163.71, 163.80. IR (Neat) ν 3398, 1575, 1506, 1417, 1217, 1049 cm^{-1}. HRMS (ESI+) $[M + H]^+$ calcd for $C_{29}H_{27}N_{10}O_2$ 547.2318; found, 547.2336. $[2\ M + H]^+$: 1093.4601.

N^2-(2,5-Dimethoxyphenyl)-N^4,N^6-diphenyl-1,3,5-triazine-2,4,6-triamine ***3b***. The title compound was synthesized from 6-chloro-N^2,N^4-diphenyl-1,3,5-triazine-2,4-diamine (**1b**) (0.74 g, 0.25 mmol) and 2,5-dimethoxyaniline (**2**) (0.078 g, 0.50 mmol) in a 1:2 ratio, following the general preparation and washing the mixture with 1 M HCl. Filtration in vacuum afforded pure **3b** as a white solid (0.099 g, 95%). mp 176−178 °C (decomp.). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 3.71 (s, 3H), 3.83 (s, 3H), 6.62 (d, J = 8.8 Hz, 1H), 6.96 (d, J = 8.8 Hz, 1H), 7.02 (t, J = 6.3 Hz, 2H), 7.28 (t, J = 6.8 Hz, 4H), 7.73 (d, J = 7.3 Hz, 4H), 7.77 (s, 1H), 7.83 (s, 1H), 9.20 (s, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 56.33, 57.26, 108.20, 109.90, 112.66, 121.53, 123.10, 129.00, 129.49, 140.29, 144.57, 154.26, 164.47, 164.67. IR (Neat) ν 3392, 1514, 1417, 1398, 1230, 1049 cm^{-1}. HRMS (ESI+) $[M + H]^+$ calcd for $C_{23}H_{23}N_6O_2$ 415.1882; found, 415.1880.

N^2-(2,5-Dimethoxyphenyl)-N^4,N^6-bis(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine ***3c***. The title compound was synthesized from 6-chloro-N^2,N^4-bis(4-methoxyphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.89 g, 0.25 mmol) and 2,5-dimethoxyaniline (**2**) (0.078 g, 0.50 mmol) in a 1:2 ratio, following the general procedure and washing the mixture with 1 M HCl. Filtration under vacuum afforded pure **3c** as a white solid (0.107 g, 90%). mp 180−181 °C (decomp.). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 3.69 (s, 3H), 3.75 (s, 6H) 3.83 (s, 3H), 6.56 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 8.8 Hz, 4H), 6.93 (d, J = 8.8 Hz, 1H), 7.47 (s, 1H), 7.58 (d, J = 8.8 Hz, 4H), 7.90 (s, 1H), 8.90 (s, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 54.98, 55.19, 56.18, 106.30, 108.05, 111.32, 113.40, 122.18, 128.85, 132.46, 142.83, 153.19, 154.70, 163.74, 164.01. IR (Neat) ν 3419, 3394, 1512, 1409, 1236, 1026 cm^{-1}. HRMS (ESI+) $[M + H]^+$ calcd for $C_{25}H_{27}N_6O_4$ 475.2094; found, 475.2108.

N-(2,5-Dimethoxyphenyl)-4,6-dipiperidino-1,3,5-triazin-2-amine ***3d***. The title compound was synthesized from 2-chloro-4,6-dipiperidino-1,3,5-triazine (**1d**) (0.070 g, 0.25 mmol) and 2,5-dimethoxyaniline (**2**) (0.078 g, 0.50 mmol) in a 1:2 ratio, following the general procedure and washing the mixture with 0.1 M HCl. Filtration under vacuum afforded pure **3d** as a white solid (0.084 g, 85%). mp 202−206 °C (decomp.). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 1.56 (m, 8H), 1.65 (m, 4H), 3.71 (s, 3H), 3.74 (t, J = 5.5 Hz, 8H), 3.82 (s, 3H), 6.61 (dd, J = 9.2, 3.3 Hz, 1H), 6.97 (d, J = 9.2 Hz, 1H), 7.89 (d, J = 3.3 Hz, 1H), 8.55 (s, 1H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 23.59, 24.92, 44.30, 55.18, 56.43, 106.73, 108.35, 112.16, 127.71, 142.97, 152.98. IR (Neat) ν 2933, 2848, 1589, 1504, 1022 cm^{-1}. HRMS (ESI+) $[M + H]^+$ calcd for $C_{21}H_{31}N_6O_2$ 399.2508; found, 399.2492.

N-(2,5-Dimethoxyphenyl)-4,6-dimorpholino-1,3,5-triazin-2-amine ***3e***. The title compound was synthesized from 2-chloro-4,6-dimorpholino-1,3,5-triazine (**1e**) (0.071 g, 0.25 mmol) and 2,5-dimethoxyaniline (**2**) (0.078 g, 0.50 mmol) in a 1:2 ratio, following the general procedure and washing the mixture with 0.1 M HCl. Filtration under vacuum afforded pure **3e** as a white solid (0.080 g, 80%). mp 201−206 °C (decomp.). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 3.61 (m, 8H), 3.69 (m, 11H), 3.80 (s, 3H), 6.51 (dd, J = 2.9, 8.8 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 7.48 (s, 1H), 7.92 (d, J = 3.4 Hz, 1H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 43.32, 55.16, 56.23, 65.93, 106.10, 106.46, 111.38, 129.04, 142.30, 152.95, 163.63, 164.57. IR (Neat) ν 3414, 1575, 1506, 1255, 1114, 1043 cm^{-1}. HRMS (ESI+) $[M + H]^+$ calcd for $C_{19}H_{27}N_6O_4$ 403.2094; found, 403.2092.

DOI: 10.1021/acssuschemeng.5b01136
ACS Sustainable Chem. Eng. 2015, 3, 3405−3411

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b01136.

NMR spectroscopy, determination of quantum yields, NMR, UV−vis, fluorescence, IR spectra, and DLS (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support is from MINECO of Spain through projects CTQ2011-22410/BQU and CTQ2014-53600-R and JCCM through project PEII-2014-002-A.

■ DEDICATION

This work is dedicated to Dr. Rajender Varma on the occasion of his 65th birthday.

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