JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

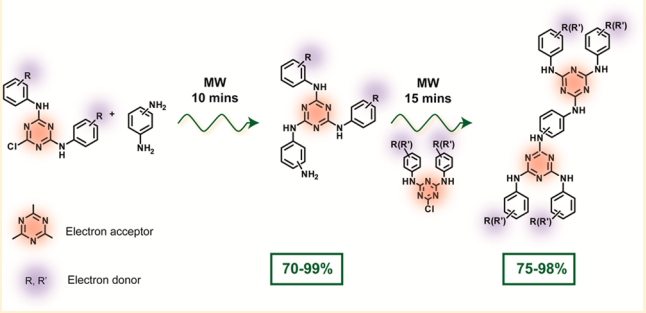
Microwave-Assisted Selective Synthesis of Mono- and Bistriazines with π-Conjugated Spacers and Study of the Optoelectronic Properties

A. Ruiz-Carretero,[†] O. Noguez,[‡] T. Herrera, J. R. Ramírez, A. Sánchez-Migallón,* and A. de la Hoz*

Departamento de Química Orgánica, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain

Supporting Information

ABSTRACT: A series of mono- and bistriazine derivatives were selectively prepared in high yields using microwave irradiation. Donor substituents were attached on the triazine ring, including pyrazolyl-substituted anilines and *o*-, *m*-, and *p*-phenylenediamine as π-conjugated spacers. This method was used to build σ−π−σ−A−σ−D systems for monotriazines and D−σ−A−σ−π−σ−A−σ−D systems for bistriazines. A study of the optoelectronic properties was performed by UV−vis and fluorescence spectroscopy and cyclic voltammetry. The monotriazines do not show any emission, but the bistriazines are blue emitters and show an interesting solvatochromic effect with large Stokes shifts of more than 10 000 cm^{-1} in some cases and quantum yields up to 23%. The optoelectronic properties depend on the conjugation and the position and donor character of the substituents and spacers. Cyclic voltammetry was used to determine the energy levels (HOMO and LUMO) in the bistriazines. An increase in the energy of the HOMO and a decrease in the energy of the LUMO were observed upon extending the conjugation. The title compounds showed interesting properties for use in optoelectronic devices, especially as blue emitters.



INTRODUCTION

π-Conjugated systems are key compounds in the field of materials chemistry because of their interesting optical and electronic properties, which result in a wide variety of applications.[1] The efficiency of optoelectronic devices based on π-conjugated systems, such as light-emitting diodes (LEDs, OLEDs, SMOLEDs), field-effect transistors (FETs), and photovoltaic cells (PVs), is based on the appropriate choice of the chemical structure, supramolecular aggregation, and electronic properties. Therefore, the construction of π-conjugated assemblies with controlled morphology and the desired properties is crucial for the fabrication of such devices.[2]

An interesting strategy to boost light absorption and tune the energy levels in π-conjugated systems is the incorporation of electron donor (D) and electron acceptor (A) moieties in the molecular design.[1,3,4] Linear and star-shaped systems can be found among the most interesting π-conjugated systems that contain D and A groups. For example, linear D−π−A−π−D or A−π−A−π−A structures have been described in systems that include azobenzenes,[5] pyridazines,[6,7] 1,2,4,5-tetrazines,[8] squarines,[9] and ferrocene.[9]

In the case of star-shaped systems, highly functionalized branches are included,[1,10] and the most interesting examples are the ones based on trisubstituted benzene rings and 1,3,5-triazines.[11−13] The introduction of nitrogen atoms has been used to replace acceptor functional groups in the benzene ring. The strong electron-acceptor character of the triazine heterocycle makes these systems comparable to D−A-substituted benzene rings.

Recently, some examples of star-shaped triazine derivatives have been reported to show good optical and electronic properties, and they have found applications in ionic liquids,[14] magnetic materials,[15] and blue-luminescent OLEDs.[16] Some of these materials were designed with a D−π−A[17] or D−π−A−π−D−π−A[18] electronic arrangement. In particular, the latter system has been shown to promote electron transport, and the derivatives synthesized according to this design exhibit large Stokes shifts, high thermal stability, and solvatochromism.[19]

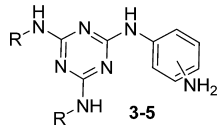
π-Conjugated systems that contain only one triazine ring have been investigated for many years.[20,21] However, bis- and bitriazine derivatives have received much less attention, despite the fact that they have interesting chemical structures that can result in new properties such as high acceptor capacity or the ability to form chelates.[22,23]

In the work described here, a new series of mono- and bistriazines was prepared using a rapid, clean, and selective method based on the use of microwave irradiation and simple purification procedures. A detailed study of the optoelectronic properties of these materials is also described, and the results

Received: February 27, 2014
Published: April 9, 2014

   dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909−4919

Table 1. Yields of Monotriazines 3−5



	R						
	Yield (%)	a	b	c	d	e	f
1,4-	3	98	70	95	98	99	86
1,3-	4	80		86	91	98	
1,2-	5			97	98	92	

highlight the potential of these structures for use in the fabrication of optoelectronic devices.

RESULTS AND DISCUSSION

Efficient procedures were applied for the preparation of bistriazine derivatives using microwave irradiation, which resulted in short reaction times and the minimum amount of solvent, with solvent-free conditions used in some cases. Furthermore, simple purification procedures were employed to obtain the final products.

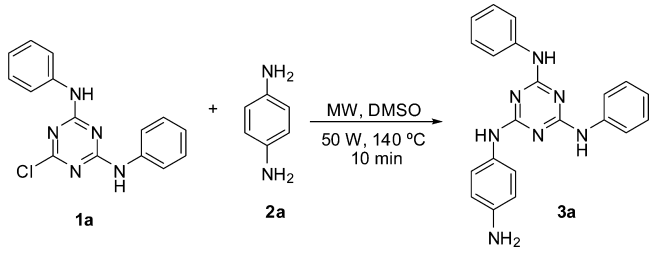
The preparation of the bistriazine derivatives presented here involved two steps. In the first step, monochlorotriazines[24] **1** were reacted with *o*-, *m*-, and *p*-phenylenediamines to yield monotriazines **3**−**5** (see Scheme 1). The second step involved the reaction of monotriazines **3**−**5** and chlorotriazines **1** to obtain bistriazines **6**−**8** (see Scheme 2). This two-step procedure allowed the preparation of symmetric and asymmetric bistriazines as well as the isolation of monotriazines. It is important to note that the third substitution in chlorotriazines always requires harsher conditions,[25] and microwave (MW) irradiation is the best energy source reported to date to carry out this substitution reaction successfully.

Monotriazines with a D−π−A−π−D structure were obtained by attaching donor substituents to the triazine π-acceptor ring. These substituents included pyrazole rings as π-donor heterocycles in order to study their influence on the optical properties and bearing in mind the interest in such compounds as ligands in coordination chemistry. Pyrazolyl substituents were introduced in different positions of the benzene ring (compounds **c**, **d**, and **e**) and were also directly attached to the aminotriazine (compounds **f**). Different donor moieties, such as *p*-methoxy groups (compounds **b**), were also attached on the molecular structure, and their effects on the optoelectronic properties were explored.

Synthesis of Monotriazines 3−5. The reaction conditions for the preparation of monotriazines **3**−**5** were optimized using the reaction between monochlorotriazine **1a**, which was previously synthesized by our group,[24] and *p*-phenylenediamine (**2a**) to give monotriazine **3a** (Scheme 1).

We previously described the reaction of chlorotriazines with 4-aminobenzylamine.[26] In this case, the different reactivity of aliphatic and aromatic amines facilitated the selective reaction

Scheme 1. Synthesis of Monotriazine 3a



with the aliphatic amine. Initially, solvent-free reactions were carried out, but complex mixtures were obtained. Small amounts of toluene, an apolar solvent that is transparent to MW irradiation, were subsequently added to the reaction mixtures. However, these conditions failed because of the low reactivity of aromatic amines. As a consequence, a polar solvent with strong MW absorption, DMSO (0.5 mL/meq), was added, and this gave the best results. In this case, a homogeneous mixture and the appropriate reaction temperature were obtained. The final optimized conditions required an excess of *p*-phenylenediamine (3 equiv) and DIPEA as the base. The reaction proved to be very clean, and pure products were obtained by simple precipitation and washing with water (Scheme 1).

The optimized conditions were applied to derivatives **3b**−**f**, and with the exception of **3b**, these reactions required harsher conditions (70 W) (Table 1). The optimized conditions were also applied to the reactions with *m*-phenylenediamine (**2b**) and *o*-phenylenediamine (**2c**) to give the corresponding monotriazines **4a**,**c**−**e** and **5c**−**e**, respectively, in excellent yields, especially when *o*-phenylenediamine was used as the spacer (Table 1).

Synthesis of Symmetric and Asymmetric Bistriazines 6−8. In this case, the conditions were optimized using the reaction affording phenyl-substituted derivative **6a** (Scheme 2). The best conditions involved the use of DMSO as the solvent (0.5 mL), DIPEA as the base, and a molar ratio of 1:1:1. The conditions of time, power, and temperature used for the preparation of monotriazines resulted in incomplete reactions, and the best results were obtained when the reactions were carried out at 170 °C for 15 min with an irradiation power of 80

dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909−4919

Scheme 2. Synthesis of Bistriazine 6a

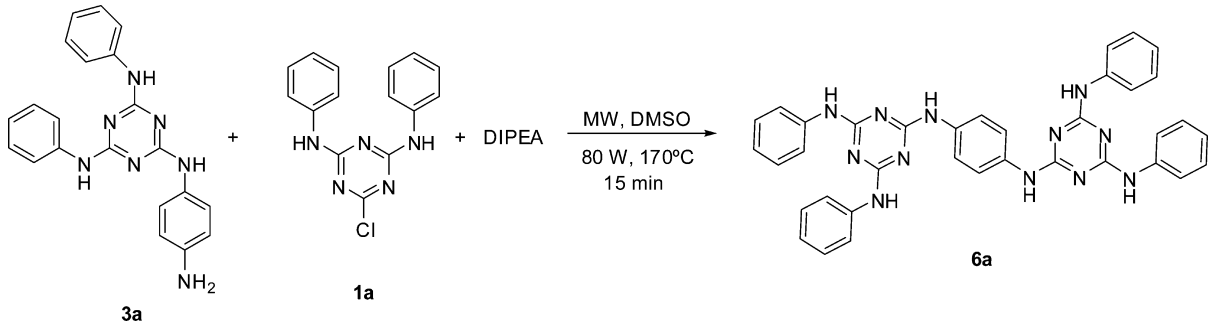
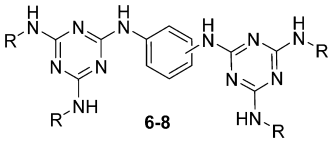


Table 2. Yields of Bistriazines 6–8



	R						
	Yield (%)	a	b	c	d	f	cd
1,4	6	97	85	80	95	97	75
							de
1,3	7			75	98		95
1,2	8			94	82		

W. The use of these conditions enabled compound **6a** to be obtained in 97% yield after precipitation and washing with water.

These conditions were extended to the preparation of symmetric and asymmetric bistriazines, which were obtained in excellent yields (Table 2). Reactions with *m*-phenylenediamine required 20 min to reach total conversion in the case of symmetric and asymmetric bistriazines (Table 2). Similarly, reactions with *o*-phenylenediamine required slightly longer reaction times (30 min) to obtain excellent yields of both mono- and bistriazines (Table 2).

Structural Determination. All of the compounds were characterized by NMR spectroscopy (^{1}H, ^{13}C, gHSQC, COSY). The ^{1}H NMR spectra at 25 °C show a complex pattern of broad signals due to the restricted rotation of the $C_{triazine}$–N bonds. The free energy of activation has been determined by our group[24,27] and others[28] to be on the order of 50–80 kJ mol^{-1}.

In the case of monotriazines, four rotamers are possible (Figure S1 in the Supporting Information). However, this number can rise to 16 in the case of the bistriazine derivatives. This situation prevents the assignment and determination of the free energy of activation of these compounds. As a consequence, the NMR spectra were recorded at high temperatures (80–125 °C) using DMSO as the solvent. At these temperatures, rotation is a rapid process and a single compound can be detected (Figure S2 in the Supporting Information).

Optical Properties. The optical properties of the mono- and bistriazines were studied in solution. The D–π–A–π–D electronic arrangement makes them very attractive for the development of compounds with interesting luminescence properties.[29]

Absorption Properties. The UV–vis spectra of monotriazines **3**–**5**, classified according to the spacer, are shown in Figure 1.

dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909–4919

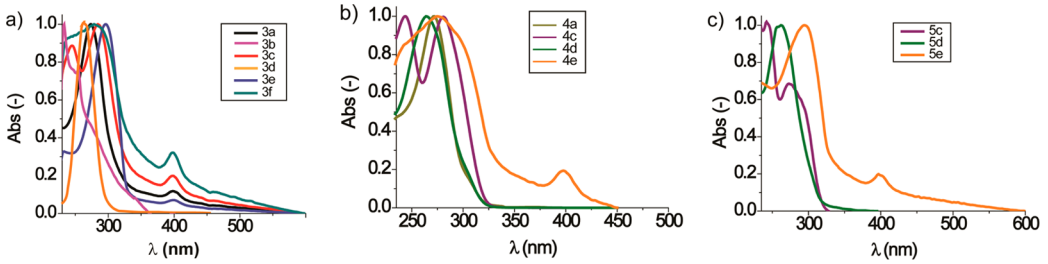
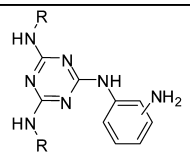


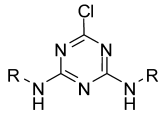
Figure 1. Normalized absorption spectra of monotriazines. Spacers: (a) *p*-phenylenediamine; (b) *m*-phenylenediamine; (c) *o*-phenylenediamine.

The absorption maxima and comparative data for the parent chlorotriazines are listed in Table 3.

Table 3. Absorption Maxima of Monotriazines 3−5



Spacer



1,4		1,3		1,2		Chlorotriazine	
λ_{max} (nm)		λ_{max} (nm)		λ_{max} (nm)		λ_{max} (nm)	
3a	274	**4a**	272			**1a**	262/277
3b	253/282					**1b**	278
3c	245/284	**4c**	244/281	**5c**	241/273	**1c**	247/289
3d	266	**4d**	264	**5d**	262	**1d**	260
3e	298	**4e**	275	**5e**	294	**1e**	274
3f	279					**1f**	255

In the case of monotriazines, the phenylenediamine spacers can be considered as donor moieties. Therefore, it can be stated that the triazine ring (acceptor) is connected to three donor substituents.

The introduction of the phenylenediamine spacers results in a slight bathochromic shift in the absorption maximum, which increases with the conjugation of the free amino group: *para* > *ortho* > *meta*. The difference between the *p*- and *o*-phenylenediamine spacers may be the result of the higher level of steric hindrance of the *ortho* substituents, leading to a decrease in the conjugation.

The incorporation of pyrazolyl groups, which are donor π-electron-rich heterocycles, as substituents on the phenyl ring generally results in a bathochromic shift when good conjugation with the spacer is allowed (compounds **3e**−**5e** and **3c**−**5c**), but this effect is almost nonexistent in derivatives with pyrazolyl substituents in the *meta* position (compounds **3d**−**5d**).

The introduction of donor groups increases the energy of the ground state. Similarly, the energy of the first excited state decreases as a result of the presence of electron-withdrawing groups. The combination of these two factors leads to a reduction in the energy gap between the ground and excited states, thus resulting in a bathochromic shift.

The main band in the absorption spectra is the result of the $\pi-\pi^*$ transition observed in π-conjugated systems. The band with the smaller extinction coefficient, at around 400 nm, could be assigned to an intramolecular charge transfer (ICT) band from the donor nitrogen atoms of the free amino groups and the pyrazolyl groups to the triazine (i.e., the acceptor).[30] However, despite the possibility that some degree of polarization may occur, it is difficult to envisage a state with total charge separation. On the other hand, it has previously been reported that donor aromatic rings may form delocalized π systems that are coplanar with other adjacent rings.[31] Such a situation would maximize the ICT and could explain the bathochromic shift.

The spectra are not consistent with an organized structure, as only broad bands are observed. This indicates the presence of monotriazine aggregates that can be formed by hydrogen bonding and $\pi-\pi$ stacking. As a consequence, *para*-substituted monotriazines (e.g., **3e**) show a broad band due to the higher conjugation and planarity, a structure that may favor stacking. In contrast, *ortho*-substituted monotriazines present two different bands. In this case, the higher level of steric hindrance probably reduces the planarity and consequently the stacking.

In derivatives **f**, the pyrazole ring is directly attached to the aminotriazine ring, and this leads to a smaller bathochromic shift as the electronic density must be shared between the triazine and benzene rings.

The introduction of a methoxy group also led to a bathochromic shift (shoulder at 282 nm) with respect to the unsubstituted derivatives **3a**−**5a**, but this shift was smaller than the one found in the compounds that contain the pyrazolyl

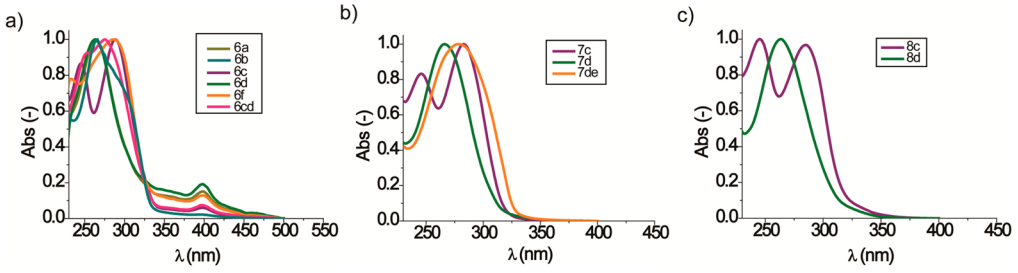


Figure 2. Normalized absorption spectra of bistriazines. Spacers: (a) *p*-phenylenediamine; (b) *m*-phenylenediamine; (c) *o*-phenylenediamine.

dx.doi.org/10.1021/jo500480r | *J. Org. Chem.* 2014, 79, 4909−4919

group. This effect is probably related to the donor capacity of the two groups, which is higher for the pyrazole ring.[32]

The UV−vis spectra of the symmetric and asymmetric bistriazines **6**−**8**, classified according to the spacer, are shown in Figure 2, and the absorption maxima are listed in Table 4. In

Table 4. Absorption Maxima of Bistriazines 6−8

1,4 spacer		1,3 spacer		1,2 spacer	
compd	λ_{max} (nm)	compd	λ_{max} (nm)	compd	λ_{max} (nm)
6a	263				
6b	266				
6c	245/288	**7c**	246/283	**8c**	245/285
6d	264	**7d**	266	**8d**	263
6f	287				
6cd	254/275	**7de**	278		

comparison to monotriazines, the extension of the conjugation in bistriazines should lead to higher extinction coefficients, and a bathochromic shift would not be expected as the distance between donor and acceptor remains constant. Experimentally, a small hypsochromic shift was observed (up to 12 nm). The main difference between mono- and bistriazines is that monotriazines have a free amino group that acts as a donor substituent. In bistriazines, this amino group is attached to the second triazine ring, which reduces its donor ability. The rest of the structural features under investigation, such as the presence of pyrazole or methoxy groups as donors, show the same trends as described above for the monotriazine derivatives.

The asymmetric bistriazine **6cd** shows a broad band with two maxima at 254 and 275 nm. The nature of this spectrum could be the result of the addition of bistriazines **6c** and **6d** with pyrazolyl groups in the *ortho* and *meta* positions, respectively.

Emission Properties. Monotriazine derivatives **3**−**5** were found to be very poor emitters in solution, with quantum yields of less than 1%. This result can be explained by strong intermolecular association formed by hydrogen bonding and π-stacking that produces fluorescence quenching.

The fluorescence spectra of bistriazines **6**−**8**, classified according to the spacer, are shown in Figure 3, and the absorption maxima are listed in Table 5. The spectroscopic features of these derivatives are compared to those of the parent chlorotriazines.

Para-substituted bistriazines **6** show an emission band at 380 nm and a second band at longer wavelengths. The latter band is due to formation of excimers,[33] which are favored by the planar disposition of these compounds.[34,35] The formation of excimers is enhanced in the pyrazolyl-substituted bistriazines, but this effect is less marked in the *meta* isomer **6d** because of the lower conjugation. A different pattern was observed when methoxy

Table 5. Emission Maxima of Bistriazines 6−8

1,4 spacer		1,3 spacer		1,2 spacer	
compd	λ_{max} (nm)	compd	λ_{max} (nm)	compd	λ_{max} (nm)
6a	380/450[b]				
6b	371[c]/434/490				
6c	385/479	**7c**	424	**8c**	438
6d	377/479[b]	**7d**	343[c]/427	**8d**	325[c]/425
6f	380/480[b]				
6cd	381/485[a]	**7de**	372[c]/408		

[a]Emission maxima of the excimer band. [b]Onset of the excimer band. [c]Shoulder.

groups were present as substituents, as in bistriazine **6b**. Two emission bands at 434 and 490 nm and a vibronic shoulder at 371 nm were observed.

The emission spectra of bistriazines **7** and **8** present a different pattern, and evidence for the formation of excimers was not observed. These spectra contain featureless broad bands, which is a sign of aggregation in the excited state.

The absorption and emission spectra do not show specular symmetry in any case. This behavior is usual in π-conjugated hydrocarbons, poly(*p*-phenylene vinylene)s, polythiophenes, and poly(*p*-phenylene)s, and it has been related to higher torsional mobility in the fundamental state compared with the first excited state. This behavior is a deviation from the Franck−Condon principle, which is applicable to the compounds discussed above. Moreover, several studies of π-conjugated polymers and oligomers have shown that restricted rotational and vibrational movements in these aggregates can be responsible for aggregation-induced emission (AIE) phenomena.[36]

Quantum Yields and Stokes Shifts. Additional data used for the determination of the quantum yields (Φ) and Stokes shifts are listed in Table 6. The quantum yields were modest, with a maximum value of 23% in the case of bistriazine **6d**, which has pyrazoles at the *meta* position and *p*-phenylenediamine as the spacer. It can be seen from Figure 3 that the formation of excimers is minimal for this derivative, and hence, there is less quenching than in the case of bistriazines **6c** and **6cd**. The Stokes shifts of the bistriazines were determined to be higher than 50 000 cm^{-1} in all cases. This behavior is typical in systems that are known to form intermolecular excimers with a high degree of aggregation.[37]

Solvatochromism. The influence of different solvents (CH_2Cl_2, CH_3CN, and MeOH) on the absorption and emission properties was studied for bistriazines **6a** and **6c**. Figure 4 shows the absorption and emission spectra of **6c** in these solvents, and Table 7 lists the absorption and emission maxima for **6a** and **6c**.

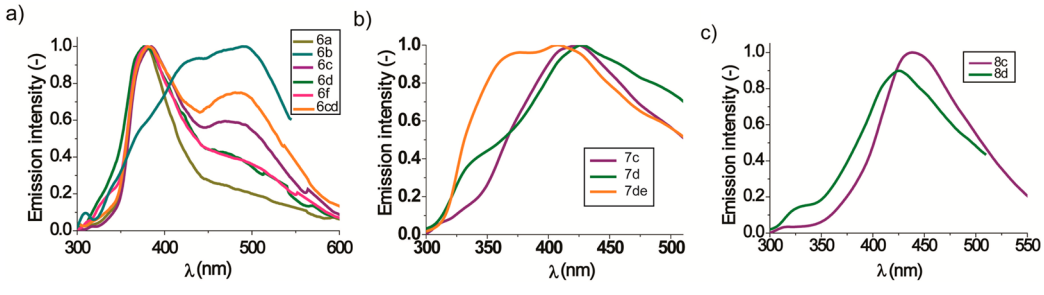


Figure 3. Normalized emission spectra of bistriazines **6**−**8**. Spacers: (a) *p*-phenylenediamine; (b) *m*-phenylenediamine; (c) *o*-phenylenediamine.

dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909−4919

Table 6. Additional Spectroscopic Data

spacer	compd	λ_{abs} (nm)	ε (10^5 M^{-1} cm^{-1})	λ_{em} (nm)	Stokes shift (cm^{-1})	Φ (%)
1,4	**6a**	263	0.47	380/450	85 470	4.4
	6b	266	2.06	434/490	44 642	0.38
	6c	245/288	1.34	385/479	103 092	4.1
	6d	264	0.43	381/450	85 470	23
	6e	287	0.53	380/450	107 520	7.3
	6cd	245/275	1.02	381/485	94 339	4.5
1,3	**7c**	246/283	2.32	424	56 179	0.77
	7d	266	2.46	339/427	62 111	2
	7de	278	2.6	372/408	76 923	1.8
1,2	**8c**	245/285	1.98	438	51 813	0.68
	8d	278	2.2	325/425	68 027	3

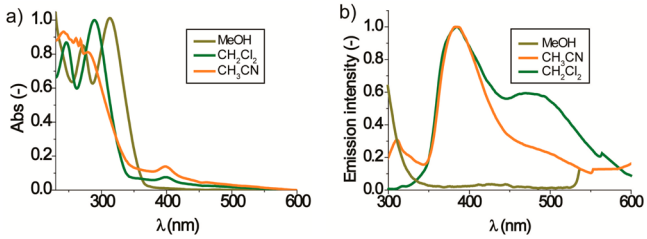


Figure 4. (a) Absorption and (b) emission spectra of compound **6c** in different solvents.

Table 7. Absorption and Emission Maxima of Compounds 6a and 6c in Different Solvents

	absorption λ_{max} (nm)		emission λ_{max} (nm)	
solvent	**6a**	**6c**	**6a**	**6c**
CH_2Cl_2	263	245/288	380/450	385/450
CH_3CN	263	244/281	385	386
CH_3OH	274	272/313	–	–

A positive solvatochromic effect was observed in the absorption spectra in going from CH_2Cl_2 to MeOH. A bathochromic shift was observed in the two absorption bands, showing some degree of polarization in the fundamental state.[38] MeOH can form hydrogen bonds with the bistriazine derivatives, favoring the charge separation and reducing the energy gap between the fundamental and excited states. However, this effect was not observed with an aprotic polar solvent, as from CH_2Cl_2 to CH_3CN a slight hypsochromic shift was observed.

Regarding the emission properties, no shifts in the emission maxima were found when the spectra were recorded in CH_2Cl_2 and CH_3CN. However, excimer formation was much higher with CH_2Cl_2, a solvent that promotes the aggregation of the bistriazines studied.

Interestingly, total quenching of the emission was found when MeOH was used as the solvent, probably due to the formation of hydrogen bonds between the solvent and the bistriazine derivatives.

The same study with bistriazine **6a** containing an unsubstituted benzene ring showed smaller effects, as expected, since the absence of the pyrazolyl group reduces the push−pull effect. These differences were observed in both the absorption and emission spectra but were especially important in the absorption spectra using methanol as the solvent. In this regard, the formation of hydrogen bonds with the pyrazole nitrogens is thought to be responsible for this dramatic effect.

It should be remarked that the quantum yields strongly depend on the polarity of the solvent, and in particular, for compound **6c** Φ increases when the polarity of the solvent increases, from only 4% in CH_2Cl_2 to 28% in CH_3CN. The use of CH_2Cl_2 promotes aggregation of these derivatives, as demonstrated by the formation of excimers, and makes them less emissive when this solvent is used.

Electrochemical Properties. A cyclic voltammetry study of the electrochemical properties of bistriazines **6**−**8** was performed in order to determine the HOMO and LUMO energies. The appropriate choice of donor and acceptor moieties can be used to tune the emission of these molecules. For instance, the attachment of a donor group at one end of the molecule may enhance the efficiency of electronic devices by increasing the energy of the HOMO and decreasing the band-gap energy.

The oxidation and reduction potentials for bistriazines **6**−**8**, the oxidation and reduction onsets, the HOMO and LUMO energies, and the band-gap energies as determined from the UV data (ΔE^{opt}) (eq S2 in the Supporting Information) and the cyclic voltammetry data (ΔE) are given in Table 8.

The ΔE^{opt} data indicate that lower band-gap energies were found when conjugation was more extended, as shown for instance by comparison of compound **6c** (pyrazole at the *ortho*

Table 8. Electrochemical Data for Bistriazines 6−8

compd	E_{ox}(onset)/E_{ox}(max)	E_{red}(onset)/E_{red}(max)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	ΔE^{opt} (eV)
6a	0.85/1.133	−0.76/−1.57	5.25	3.64	1.61	2.49
6c	1.01/1.208	−0.8/−1.10	5.41	3.60	1.81	2.47
6d	0.83/1.124	−0.42/−0.74	5.23	3.98	1.25	2.50
6f	0.79/0.94	–	5.19	–	–	2.46
6cd	0.70/1.136	−0.47/−0.80	5.10	3.93	1.17	2.49
7c	0.74/0.982	−0.51/−1.04	5.14	3.99	1.15	3.09
7d	0.81/1.121	−0.75/−1.20	5.21	3.65	1.56	3.19
8c	0.85/1.040	−0.40/−0.673, 1.164	5.25	4	1.25	3.3
8d	0.33/1.173	−0.39/−0.74, 1.115	4.73	3.01	1.72	3.09

dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909−4919

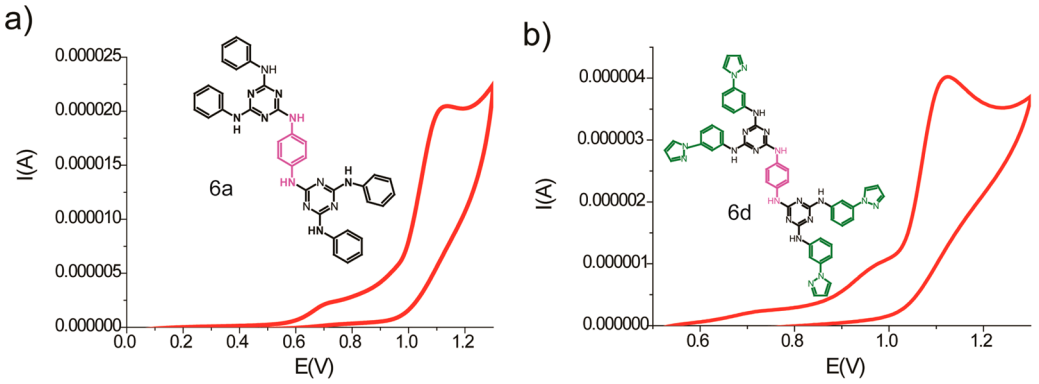


Figure 5. Oxidation curves for bistriazines (a) **6a** and (b) **6d**.

position) with **6d** (pyrazole at the *meta* position) or compound **6e** (*para* substitution) with compounds **7d** (*meta* substitution) and **8c** (*ortho* substitution).

Similarly, the HOMO energies were higher for triazines with more extensive conjugation, where the oxidation process requires more energy. When the substituent is at the *meta* position or *m*-phenylenediamine is used as the spacer, the conjugation is less extensive and the oxidation process occurs more easily.

As far as the LUMO energies are concerned, derivatives with a higher degree of conjugation had lower LUMO energies, facilitating the reduction processes. LUMOs that are higher in energy were calculated for derivatives with donor substituents in the *meta* position or those in which *m*-phenylenediamine is the spacer.

Compound **6a**, which contains unsubstituted phenyl rings, has HOMO and LUMO energies with intermediate values with respect to the *para*- and *meta*-substituted derivatives.

The differences between the electrochemical and optical values can be explained by the different solvents (acetonitrile vs dichloromethane) and concentrations used in each technique.

Considering the possible electronic and photovoltaic applications, compounds with a lower energy gap (lower LUMO and higher HOMO) should be more appropriate.

Oxidation curves for bistriazines **6**–**8** were irreversible in all cases. As an example, the oxidation curves for bistriazines **6a** and **6d** are shown in Figure 5. Only one maximum was observed for compound **6a** (phenyl-substituted), while for compound **6c** (*m*-pyrazolyl), a second band with lower intensity and at lower oxidation potential was observed. The reduction curves were irreversible in most cases, except for some derivatives such as bistriazine **6d** (Figure 6).

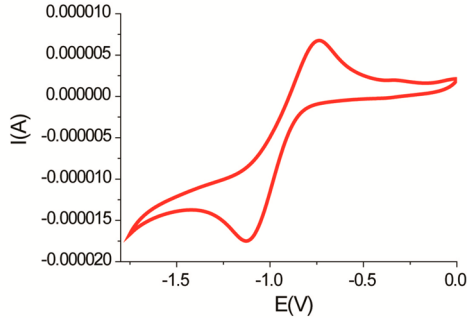


Figure 6. Reduction curves for bistriazine **6d**.

CONCLUSIONS

A series of mono- and bistriazine derivatives was prepared by reaction of chlorotriazines with *o*-, *m*-, and *p*-phenylenediamine. The reactions were performed selectively using microwave irradiation, short reaction times, a minimum amount of solvent, and simple purification procedures. This method is very versatile and allows the selective preparation of monotriazines and symmetric and asymmetric bistriazines.

These compounds showed interesting optoelectronic and electrochemical properties, with clear differences observed between the mono- and bistriazines, different spacers, and the presence of donor substituents. The electronic properties depend on the solvent used, and solvatochromism was observed. This behavior was especially marked when methanol was used as the solvent, resulting in a large bathochromic shift (200 nm) and high quantum yields (28%). The interesting properties of these mono- and bistriazine derivatives open the way to possible applications in the field of optoelectronic devices.

EXPERIMENTAL SECTION

General. All of the reagents and solvents were commercial grade and used without further purification. Melting points were obtained with an SMP3 apparatus without correction. Thin-layer chromatograms were obtained on AL silica gel 60 F254 from Merck. Reactions were performed in a microwave monomode reactor (CEM, Discover) at ambient pressure, and the reaction temperatures were measured with an infrared pyrometer.

NMR spectra were recorded in DMSO-d_6 on NMR spectrometers operating at 499.980 and 299.98 MHz for ^{1}H and at 125.423 and 75.42 MHz for ^{13}C. IR spectra were recorded on an IR spectrophotometer provided with an attenuated total reflectance (ATR) accessory. Mass spectra were recorded with FAB ionization in the positive mode and a magnetic sector mass analyzer (FAB-B). UV–vis and fluorescence spectra were recorded at ambient temperature using spectroscopic grade dichloromethane and a concentration of 5.5×10^{-6} M for absorbance and 10^{-6} M for fluorescence. Cyclic voltammetry was carried out using a platinum working electrode, a Ag/AgCl reference electrode, and a platinum counter electrode. Degassed acetonitrile was used as the solvent and a 0.1 mM solution of Bu_4NPF_6 as the supporting electrolyte. The sweep speed was 100 mV/s.

Preparation of Monotriazines 3–5. The spacer (*o*-, *m*-, or *p*-phenylenediamine), the appropriate chlorotriazine **2** (0.3 mmol), and diisopropylethylamine (DIPEA) in a 3:1:1 ratio were dissolved in anhydrous DMSO. The mixture was introduced into a microwave flask fitted with a reflux condenser and a silica gel tube under argon. The mixture was subjected to microwave irradiation at ambient pressure for 10 min (20 min with *o*-phenylenediamine) at 50 W (70 W for *p*-methoxyphenyl) and 140 °C. The mixture was washed with water (3 × 2 mL) and filtered to give the pure product.

dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909–4919

*N-4-Aminophenyl-N′,N″-diphenyl-1,3,5-triazine-2,4,6-triamine (**3a**).* From 6-chloro-*N*,*N*′-diphenyl-1,3,5-triazine-2,4-diamine (**1a**) (0.3 mmol, 0.0897 g), *p*-phenylenediamine (**2a**) (0.9 mmol, 0.097 g), DIPEA (0.3 mmol, 0.039 g), and DMSO (0.5 mL). White solid, 0.100 g (98%), mp 201−205 °C (decomp). ^{1}H NMR (25 °C, 500 MHz, DMSO) δ 4.82 (bs, 2H), 6.55 (d, J = 7.8 Hz, 2H), 6.96 (t, J = 7.07 Hz, 2H), 7.26 (t, J = 6.55 Hz, 4H), 7.33 (d, J = 7.32 Hz, 2H), 7.80 (bs, 4H), 8.79 (bs, 1H), 9.08 (bs, 2H, NH). ^{13}C NMR (25 °C, 125 MHz, DMSO) δ 113.8, 120.1, 121.7, 123.0, 128.3, 128.6, 140.2, 144.4, 164.1, 164.2. IR (neat) ν 3388, 3265, 1575, 1514, 1415 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 274 (0.81). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{21}H_{20}N_7$ 370.1780, found 370.1755.

*N-4-Aminophenyl-N′,N″-bis(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine (**3b**).* From 6-chloro-*N*,*N*′-bis(4-methoxyphenyl)-1,3,5-triazine-2,4-diamine (**1b**) (0.5 mmol, 0.178 g), *p*-phenylenediamine (**2a**) (1.5 mmol, 0.162 g), DIPEA (0.5 mmol, 0.087 g), and DMSO (0.5 mL). White solid, 0.150 g (70%), mp 85−89.4 °C (decomp). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 3.75 (s, 6H), 4.59 (bs, 2H), 6.55 (d, J = 8.78 Hz, 2H), 6.86 (d, J = 9.27 Hz, 4H), 7.32 (d, J = 8.78 Hz, 2H), 7.63 (d, J = 9.27 Hz, 4H), 8.4 (bs, 1H), 8.62 (bs, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 55.0, 113.3, 113.6, 121.8, 122.5, 128.8, 133.0, 143.8, 154.4, 164.0, 164.1. IR (neat) ν 3383, 1573, 1512, 1232 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 253, 282 (8.3). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{23}H_{24}N_7O_2$ 430.1991, found 430.1983.

*N-4-Aminophenyl-N′,N″-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**3c**).* From 6-chloro-*N*,*N*′-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.3 mmol, 0.0897 g), *p*-phenylenediamine (**2a**) (0.9 mmol, 0.097 g), DIPEA (0.3 mmol, 0.039 g), and DMSO (0.5 mL). White solid, 0.09 g (95%), mp 107−111 °C. ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 4.65 (bs, 2H), 6.52 (d, J = 8.29 Hz, 2H), 6.54 (t, J = 2.19 Hz, 2H), 7.18 (t, J = 7.56 Hz, 2H), 7.22 (d, J = 8.78 Hz, 2H), 7.35 (t, J = 7.56 Hz, 2H), 7.50 (dd, J = 8.29 and 1.22 Hz, 2H), 7.84 (d, J = 1.95 Hz, 2H), 8.16 (d, J = 2.44 Hz, 2H), 8.31 (d, J = 8.29 Hz, 2H), 8.85 (bs, 1H), 9.24 (bs, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 106.6, 113.5, 122.3, 123.0, 123.4, 123.9, 127.0, 128.2, 130.1, 130.8, 131.9, 140.5, 144.0, 163.9, 163.9. IR (neat) ν 3311, 1504, 1415 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 245, 284 (0.5). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2214.

*N-4-Aminophenyl-N′,N″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**3d**).* From 6-chloro-*N*,*N*′-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1d**) (0.1 mmol, 0.043 g), *p*-phenylenediamine (**2a**) (0.3 mmol, 0.039 g), DIPEA (0.1 mmol, 0.0129 g), and DMSO (0.5 mL). White solid, 0.099 g (99%), mp 107−110 °C. ^{1}H NMR (300 MHz, 80 °C, DMSO) δ 4.60 (s, 2H), 6.50−6.54 (m, 3H), 7.31 (t, J = 8.35 Hz, 4H), 7.41 (pseudo d, J = 8.13 Hz, 2H), 7.7 (d, J = 1.76 Hz, 2H), 7.79 (d, J = 8.13 Hz, 2H), 8.1 (t, J = 1.97 Hz, 2H), 8.21 (d, J = 2.42 Hz, 2H), 8.61 (bs, 1H), 9.05 (bs, 2H). ^{13}C NMR (75 MHz, 80 °C, DMSO) δ 107.1, 110.3, 112.0, 113.7, 117.9, 123.1, 127.2, 128.2, 128.8, 139.7, 140.2, 140.8, 144.2, 164.0, 164.2. IR (neat) ν 3284, 1581, 1514, 1413 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 266 (0.8). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2220.

*N-4-Aminophenyl-N′,N″-bis(4-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**3e**).* From 6-chloro-*N*,*N*′-bis(4-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1e**) (0.1 mmol, 0.043 g), *p*-phenylenediamine (**2a**) (0.3 mmol, 0.039 g), DIPEA (0.1 mmol, 0.0129 g), and DMSO (0.5 mL). White solid, 0.099 g (99%), mp 135−138.2 °C. ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 4.66 (bs, 2H), 6.49 (t, J = 1.95 Hz, 2H), 6.59 (d, J = 8.29 Hz, 2H), 7.32 (d, J = 8.29 Hz, 2H), 7.69 (m, 6H), 7.9 (d, J = 8.78 Hz, 4H), 8.31 (d, J = 2.44 Hz, 2H), 8.61 (bs, 1H), 9.02 (bs, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 107.0, 113.7, 118.5, 120.6, 123.0, 127.0, 128.4, 134.1, 138.2, 140.0, 144.2, 163.9, 164.2. IR (neat) ν 1575, 1487, 1409 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 279 (1.5). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2209.

*N-4-Aminophenyl-N′,N″-bis(1-phenyl-1H-pyrazol-4-yl)-1,3,5-triazine-2,4,6-triamine (**3f**).* From 6-chloro-*N*,*N*′-bis(1-phenyl-1*H*-pyrazol-4-yl)-1,3,5-triazine-2,4-diamine (**1f**) (0.23 mmol, 0.1 g), *p*-phenylenediamine (**2a**) (0.7 mmol, 0.075 g), DIPEA (0.23 mmol, 0.04 g), and DMSO (0.5 mL). White solid, 0.099 g (86%), mp 131−134.5 °C. ^{1}H NMR (500 MHz, 95 °C, DMSO) δ 4.71 (bs, 2H), 6.64 (d, J = 8.29 Hz, 2H), 7.26 (m, 4H), 7.5 (s, 4H), 7.73 (s, 4H), 7.82 (s, 2H), 8.56 (bs, 3H), 8.97 (bs, 2H). ^{13}C NMR (125 MHz, 95 °C, DMSO) δ 113.8, 116.9, 117.5, 124.0, 124.8, 125.1, 128.3, 129.0, 133.2, 139.7, 144.5, 163.4, 165.0. IR (neat) ν 3078, 1556, 1504, 1394 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 298 (0.31). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2144.

*N-3-Aminophenyl-N′,N″-diphenyl-1,3,5-triazine-2,4,6-triamine (**4a**).* From 6-chloro-*N*,*N*′-diphenyl-1,3,5-triazine-2,4-diamine (**1a**) (0.3 mmol, 0.0897 g), *m*-phenylenediamine (**2b**) (0.9 mmol, 0.097g), DIPEA (0.3 mmol, 0.039 g), and DMSO (0.5 mL). White solid, 0.100 g (98%), mp 107 °C (decomp). ^{1}H NMR (500 MHz, 25 °C, DMSO) δ 4.88 (bs, 2H), 6.25 (d, J = 6.83 Hz, 1H), 6.9−7.0 (m, 5H), 7.28 (t, J = 8.05 Hz, 4H), 7.81 (d, J = 7.81 Hz, 4H), 8.95 (bs, 1H), 9.14 (s, 2H). ^{13}C NMR (125 MHz, 25 °C, DMSO) δ 106.8, 108.7, 109.2, 120.2, 121.8, 128.3, 128.6, 140.0, 140.2, 148.6, 164.1, 164.1. IR (neat) ν 3390, 3275, 1574, 1416 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 272 (1.76). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{21}H_{20}N_7$ 370.1780, found 370.1767.

*N-3-Aminophenyl-N′,N″-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**4c**).* From 6-chloro-*N*,*N*′-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.3 mmol, 0.128 g), *m*-phenylenediamine (**2b**) (0.9 mmol, 0.097 g), DIPEA (0.3 mmol, 0.039 g), and DMSO (0.5 mL). White solid, 0.129 g (86%), mp 107−111 °C. ^{1}H NMR (500 MHz, 25 °C, DMSO) δ 4.88 (bs, 2H), 6.24 (d, J = 7.32 Hz, 1H), 6.56 (bs, 2H), 6.78−6.86 (m, 2H), 6.88 (pseudo t, J = 7.81 Hz, 1H), 7.22 (t, J = 7.56 Hz, 2H), 7.39 (t, J = 7.56 Hz, 2H), 7.54 (d, J = 7.81 Hz, 2H), 7.88 (d, J = 1.4 Hz, 2H), 8.23 (d, J = 1.95 Hz, 2H), 8.29 (bs, 2H), 9.25 (s, 1H), 9.51 (bs, 2H). ^{13}C NMR (125 MHz, 25 °C, DMSO) δ 106.5, 107.1, 108.8, 108.9, 123.7, 124.6, 127.4, 128.5, 130.6, 131.3, 131.7, 139.9, 141.0, 148.6, 164.1, 164.1. IR (neat) ν 3306, 1504, 1446, 1411 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 244, 281 (1.68). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2206.

*N-3-Aminophenyl-N′,N″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**4d**).* From 6-chloro-*N*,*N*′-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1d**) (0.23 mmol, 0.098 g), *m*-phenylenediamine (**2b**) (0.7 mmol, 0.075 g), DIPEA (0.23 mmol, 0.037 g), and DMSO (0.5 mL). White solid, 0.105 g (91%), mp 111 °C. ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 4.7 (bs, 2H), 6.29 (d, J = 7.8 Hz, 1H), 6.5 (t, J = 1.95 Hz, 2H), 6.88 (t, J = 7.8 Hz, 1H), 6.95−6.98 (m, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.43 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 1.95 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 8.1 (d, J = 1.95 Hz, 2H), 8.26 (d, J = 2.44 Hz, 2H), 8.8 (s, 1H), 9.1 (bs, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 107.0, 107.1, 108.9, 109.5, 110.5, 112.2, 118.1. 127.2, 128.2, 128.9, 139.7, 139.7, 140.3, 140.6, 148.2, 164.0, 164.1. IR (neat) ν 3388, 3288, 1583, 1409 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 264 (0.88). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2208.

*N-3-Aminophenyl-N′,N″-bis(4-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**4e**).* From 6-chloro-*N*,*N*′-bis(4-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1e**) (0.25 mmol, 0.1073 g), *m*-phenylenediamine (**2b**) (0.75 mmol, 0.078 g), DIPEA (0.25 mmol, 0.039 g), and DMSO (0.5 mL). White solid, 0.125 g (99%), mp 118−119 °C. ^{1}H NMR (500 MHz, 120 °C, DMSO) δ 4.57 (bs, 2H), 6.34 (dd, J = 1.46 and 6.34 Hz, 1H), 6.49 (dd, J = 1.95 and 2.44 Hz, 2H), 6.91−7.0 (m, 2H), 7.03 (m, 1H), 7.68 (d, J = 9.27 Hz, 6H), 7.88 (d, J = 9.27 Hz, 4H), 8.25 (d, J = 2.44 Hz, 2H), 8.52 (bs, 1H), 8.87 (bs, 2H). ^{13}C NMR (125 MHz, 120 °C, DMSO) δ 106.5, 107.1, 108.9, 109.5, 118.4, 120.7, 126.7, 127.9, 134.3, 137.8, 139.6, 139.7, 147.9, 163.9, 164.1. IR (neat) ν 3389, 1581, 1524, 1410 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 275 (0.37). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2196.

*N-2-Aminophenyl-N′,N″-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**5c**).* From 6-chloro-*N*,*N*′-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.14 mmol, 0.06 g), *o*-phenylenediamine (**2c**) (0.42 mmol, 0.045 g), DIPEA (0.14 mmol, 0.026 g), and DMSO (0.5 mL). White solid, 0.065 g (97%), mp 107−111 °C. ^{1}H NMR (500 MHz, 25 °C, DMSO) δ 4.85 (s, 2H), 6.56 (m, 3H), 6.73 (d, J = 7.81 Hz, 1H), 6.91 (t, J = 7.81 Hz, 1H), 7.18 (pseudo t, J = 6.10 Hz, 3H), 7.28 (m, 2H), 7.49 (d, J = 8.78 Hz, 2H), 7.87 (s, 2H), 8.21 (s, 2H), 8.28 (m, 2H), 8.62 (s, 1H), 9.43 (s, 2H). ^{13}C NMR (125 MHz, 25 °C, DMSO) δ 107.2, 115.6, 115.9, 123.3, 123.6, 123.7, 124.1, 125.8, 126.9, 127.4, 131.4, 131.9, 141.0, 142.9, 164.1, 165.2. IR (neat) ν 3290, 1574,

dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909−4919

1704, 1414 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 241, 273 (0.2). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2203.

*N-2-Aminophenyl-N′,N″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**5d**).* From 6-chloro-*N*,*N*′-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1d**) (0.23 mmol, 0.098 g), *o*-phenylenediamine (**2c**) (0.7 mmol, 0.075 g), DIPEA (0.23 mmol, 0.037 g), and DMSO (0.5 mL). White solid, 0.113 g (98%), mp 105−106 °C. ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 4.75 (bs, 2H), 6.49 (t, J = 2.19 Hz, 2H), 6.56 (t, J = 6.83 Hz, 1H), 6.77 (d, J = 7.32 Hz, 1H), 6.93 (t, J = 7.32 Hz, 1H), 7.28 (t, J = 8.05 Hz, 3H), 7.39 (d, J = 8.29 Hz, 2H), 7.69 (d, J = 1.46 Hz, 2H), 7.76 (d, J = 7.81 Hz, 2H), 8.10 (s, 2H), 8.17 (bs, 2H), 8.27 (s, 1H), 9.14 (s, 2H). ^{13}C NMR (75 MHz, 80 °C, DMSO) δ 107.1, 110.2, 112.0, 115.6, 116.1, 117.8, 123.9, 125.6, 126.7, 127.2, 128.8, 139.6, 140.2, 140.7, 142.8, 164.1, 165.1. IR (neat) ν 3290, 1580, 1504, 1414 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 262 (1.37). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2216.

*N-2-Aminophenyl-N′,N″-bis(4-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**5e**).* From 6-chloro-*N*,*N*′-bis(4-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1e**) (0.25 mmol, 0.1073 g), *o*-phenylenediamine (**2c**) (0.75 mmol, 0.078 g), DIPEA (0.25 mmol, 0.039 g), and DMSO (0.5 mL). White solid, 0.115 g (92%), mp 154 °C. ^{1}H NMR (500 MHz, 95 °C, DMSO) δ 4.68 (bs, 2H), 6.48 (t, J = 2.19 Hz, 2H), 6.65 (t, J = 7.56 Hz, 1H), 6.82 (d, J = 8.29 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 7.81 Hz, 1H), 7.64 (d, J = 8.78 Hz, 4H), 7.68 (d, J = 1.95 Hz, 2H), 7.87 (d, J = 8.78 Hz, 4H), 8.14 (bs, 1H), 8.27 (d, J = 2.44 Hz, 2H), 8.99 (bs, 2H). ^{13}C NMR (125 MHz, 95 °C, DMSO) δ 106.7, 115.6, 116.1, 118.4, 120.5, 124.1, 125.4, 126.7, 126.8, 134.1, 138.1, 139.8, 142.7, 164.0, 165.2. IR (neat) ν 3396, 3286, 1521, 1487, 1410 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 294 (1.05). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{27}H_{24}N_{11}$ 502.2216, found 502.2196.

Preparation of Bistriazines 6−8. The synthesis of bistriazines was similar to the preparation of monotriazines, using the appropriate chlorotriazine **1**, monotriazine **3**−**5**, and diisopropylethylamine (DIPEA) in a 1:1:1 ratio and anhydrous DMSO (0.5 mL) as the solvent. The mixture was irradiated under argon for 15 min for **6**, 20 min for **7** and 30 min for **8** at 170 °C and 80 W. The crude product was washed with water (2 × 3 mL) and filtered to give the pure product.

*N,N′-Bis[4,6-bis(phenylamino)-1,3,5-triazin-2-yl]-p-phenylenediamine (**6a**).* From *N*-4-aminophenyl-*N*′,*N*″-diphenyl-1,3,5-triazine-2,4,6-triamine (**3a**) (0.5 mmol, 0.185 g), 6-chloro-*N*,*N*′-diphenyl-1,3,5-triazine-2,4-diamine (**1a**) (0.5 mmol, 0.148 g), DIPEA (0.5 mmol, 0.065 g), and DMSO (0.5 mL). White solid, 0.306 g (97%), mp 150 °C (decomp). ^{1}H NMR (500 MHz, 25 °C, DMSO) δ 6.98 (t, J = 7.32 Hz, 4H), 7.28 (t, J = 7.81 Hz, 8H), 7.72 (s, 4H), 7.82 (d, J = 6.83 Hz, 8H), 9.17 (s, 2H), 9.20 (s, 4H). ^{13}C NMR (125 MHz, 25 °C, DMSO) δ 120.2, 120.7, 121.9, 128.3, 134.5, 140.0, 164.0, 164.1. IR (neat) ν 3402, 3287, 1574, 1493, 1410 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 263 (0.47). MS (FAB) $[M + H]^+$ m/z calcd for $C_{36}H_{31}N_{12}$ 631.2795, found 631.2828.

*N,N′-Bis[4,6-bis(4-methoxyphenylamino)-1,3,5-triazin-2-yl]-p-phenylenediamine (**6b**).* From *N*-4-aminophenyl-*N*′,*N*″-bis(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine (**3b**) (0.23 mmol, 0.1 g), 6-chloro-*N*,*N*′-bis(4-methoxyphenyl)-1,3,5-triazine-2,4-diamine (**1b**) (0.23 mmol, 0.08 g), DIPEA (0.23 mmol, 0.036 g), and DMSO (0.5 mL). White solid, 0.146 g (85%), mp 111−114 °C (decomp). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 3.74 (s, 12H), 6.86 (d, J = 8.78 Hz, 8H), 7.64 (m, 12H), 8.72 (s, 4H), 8.78 (s, 2H). ^{13}C NMR (75 MHz, 80 °C, DMSO) δ 55.0, 113.4, 120.4, 122.0, 132.8, 134.2, 154.6, 163.9, 164.0. IR (neat) ν 3404, 1574, 1495, 1410 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 266 (2.06). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{40}H_{39}N_{12}O_4$ 751.3217, found 751.3218.

*N,N′-Bis[4,6-bis(2-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-p-phenylenediamine (**6c**).* From *N*-4-aminophenyl-*N*′,*N*″-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**3c**) (0.18 mmol, 0.09 g), 6-chloro-*N*,*N*′-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.18 mmol, 0.077 g), DIPEA (0.18 mmol, 0.026 g), and DMSO (0.5 mL). White solid, 0.127 g (80%), mp 170−172.5 °C (decomp). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 6.54 (t, J = 2.19 Hz, 4H), 7.21 (t, J = 7.81 Hz, 4H), 7.37 (t, J = 8.5 Hz, 4H), 7.53 (m, 8H), 7.84 (d, J = 1.95 Hz, 4H), 8.17 (d, J = 2.44 Hz, 4H), 8.3 (d, J = 8.29 Hz, 4H), 9.2 (bs, 2H), 9.36 (bs, 4H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 106.6, 120.4, 123.3, 123.4, 124.2, 127.0, 130.5, 130.8, 131.7, 134.0, 140.5, 163.9, 164.0. IR (neat) ν 3286, 1726, 1658, 1523 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 245, 288 (1.34). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3678.

*N,N′-Bis[4,6-bis(3-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-p-phenylenediamine (**6d**).* From *N*-4-aminophenyl-*N*′,*N*″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**3d**) (0.13 mmol, 0.063 g), 6-chloro-*N*,*N*′-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1d**) (0.13 mmol, 0.056 g), DIPEA (0.13 mmol, 0.016 g), and DMSO (0.5 mL). White solid, 0.110 g (95%), mp 165−168 °C (decomp). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 6.49 (t, J = 1.95 Hz, 4H), 7.34 (t, J = 8.05 Hz, 4H), 7.42 (d, J = 8.29 Hz, 4H), 7.65 (s, 4H), 7.70 (d, J = 1.46 Hz, 4H), 7.83 (d, J = 7.32 Hz, 4H), 8.12 (d, J = 1.95 Hz, 4H), 8.25 (d, J = 2.44 Hz, 4H), 9.02 (bs, 2H), 9.22 (bs, 4H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 107.1, 110.6, 112.2, 118.1, 120.9, 127.2, 128.9, 134.2, 139.7, 140.3, 140.7, 164.0, 164.1. IR (neat) ν 3400, 3277, 1583, 1487, 1408 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 264 (0.43). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3666.

*N,N′-Bis[4,6-bis(1-phenyl-1H-pyrazol-4-ylamino)-1,3,5-triazin-2-yl]-p-phenylenediamine (**6f**).* From *N*-4-aminophenyl-*N*′,*N*″-bis(1-phenyl-1*H*-pyrazol-4-yl)-1,3,5-triazine-2,4,6-triamine (**3f**) (0.19 mmol, 0.099 g), 6-chloro-*N*,*N*′-bis(1-phenyl-1*H*-pyrazol-4-yl)-1,3,5-triazine-2,4-diamine (**1f**) (0.19 mmol, 0.082 g), DIPEA (0.19 mmol, 0.034 g), and DMSO (0.5 mL). White solid, 0.165 g (97%), mp 117−121 °C (decomp). ^{1}H NMR (500 MHz, 120 °C, DMSO) δ 7.24 (t, J = 6.8 Hz, 4H), 7.45 (t, J = 7.06 Hz, 8H), 7.74 (m, 12H), 7.88 (s, 4H), 8.58 (s, 4H), 8.9−9.1 (m, 6H). ^{13}C NMR (125 MHz, 120 °C, DMSO) δ 117.1, 117.5, 121.4, 124.5, 125.0, 128.7, 133.4, 134.4, 139.6, 163.5, 164.47. IR (neat) ν 3408, 3284, 1556, 1495, 1396 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 287 (20.53). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3678.

*N-[4,6-Bis(3-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-N′-[4,6-bis(2-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-p-phenylenediamine (**6cd**).* From *N*-4-aminophenyl-*N*′,*N*″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**3d**) (0.12 mmol, 0.06 g), 6-chloro-*N*,*N*′-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.12 mmol, 0.051 g), DIPEA (0.12 mmol, 0.015 g), and DMSO (0.5 mL). White solid, 0.08 g (75%), mp 120.3−122 °C (decomp). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 6.47−6.54 (m, 4H), 7.21 (t, J = 7.56 Hz, 2H), 7.3−7.44 (m, 6H), 7.5−7.7 (m, 8H), 7.76−7.88 (m, 4H), 8.1−8.2 (m, 4H), 8.22−8.32 (m, 4H), 9.0−9.4 (m, 6H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 106.7, 107.2, 110.5, 112.2, 118.1, 120.4, 121.0, 123.3, 123.5, 124.3, 127.0, 127.2, 129.0, 130.5, 130.9, 131.7, 134.1, 134.1, 139.8, 140.3, 140.5, 140.7, 163.9, 164.0, 164.1. IR (neat) ν 3395, 3304, 1580, 1485, 1408 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 254, 275 (1.02). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3684.

*N,N′-Bis[4,6-bis(2-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-m-phenylenediamine (**7c**).* From *N*-3-aminophenyl-*N*′,*N*″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**4c**) (0.12 mmol, 0.06 g), 6-chloro-*N*,*N*′-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.12 mmol, 0.051 g), DIPEA (0.12 mmol, 0.015 g), and DMSO (0.5 mL). White solid, 0.08 g (75%), mp 138−139 °C. ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 6.5 (t, J = 2.19 Hz, 4H), 7.15 (m, 7H), 7.31 (t, J = 7.57 Hz, 4H), 7.5 (dd, J = 8.29 and 1.22 Hz, 4H), 7.81 (d, J = 1.46 Hz, 4H), 8.02 (t, J = 1.95 Hz, 1H), 8.11 (d, J = 2.44 Hz, 4H), 8.27 (d, J = 7.69 Hz, 4H), 9.14 (bs, 2H), 9.34 (bs, 4H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 106.6, 113.7, 115.0, 123.2, 123.3, 124.1, 126.9, 127.4, 130.4, 130.7, 131.6, 139.0, 140.4, 163.9, 164.0. IR (neat) ν 3277, 1504, 1447, 1408 cm^{-1}. UV λ_{max}/nm ($\varepsilon/10^5$ mol L^{-1} cm^{-1}) 246, 283 (2.32). MS (FAB-B) m/z $[M + H]^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3678.

*N,N′-Bis[4,6-bis(3-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-m-phenylenediamine (**7d**).* From *N*-3-aminophenyl-*N*′,*N*″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**4d**) (0.21 mmol, 0.105 g), 6-chloro-*N*,*N*′-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1d**) (0.21 mmol, 0.09 g), DIPEA (0.21 mmol, 0.03 g), and DMSO (0.5 mL). White solid, 0.186 g (98%), mp 104−105 °C (decomp). ^{1}H NMR (500 MHz, 95 °C, DMSO) δ 6.48 (bs, 4H), 7.08 (t, J = 8.29 Hz, 1H), 7.33 (m, 5H), 7.41 (d, J = 8.29 Hz, 4H), 7.48 (d, J = 7.81 Hz, 1H), 7.69 (bs, 4H), 7.81 (d, J = 8.29 Hz, 4H), 8.02 (s, 1H), 8.09 (s, 4H), 8.23

dx.doi.org/10.1021/jo500480r | J. Org. Chem. 2014, 79, 4909−4919

(bs, 4H), 8.89 (s, 2H), 9.15 (bs, 4H). ^{13}C NMR (125 MHz, 95 °C, DMSO) δ 107.1, 110.7, 111.5, 112.3, 115.5, 118.2, 127.2, 127.3, 128.9, 139.3, 139.8, 140.3, 140.5, 164.1. IR (neat) ν 3397, 3290, 1583, 1454, 1408 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 266 (2.46). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3656.

*N-[4,6-bis(3-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-N′-[4,6-bis(4-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-m-phenylenediamine (**7de**).* From *N*-3-aminophenyl-*N*′,*N*″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**4d**) (0.19 mmol, 0.085 g), 6-chloro-*N*,*N*′-bis(4-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1e**) (0.19 mmol, 0.10 g), DIPEA (0.19 mmol, 0.027 g), and DMSO (0.5 mL). White solid, 0.081 g (95%), mp 104−105 °C (decomp). ^{1}H NMR (500 MHz, 80 °C, DMSO) δ 6.49−6.51 (m, 4H), 7.18 (t, J = 8.08 Hz, 1H), 7.33 (t, J = 8.05 Hz, 2H), 7.41 (d, J = 9.27 Hz, 2H), 7.46 (d, J = 8.79 Hz, 1H), 7.50 (pseudo t, J = 6.83 Hz, 1H), 7.6−7.75 (m, 8H), 7.84 (d, J = 8.29 Hz, 2H), 7.91 (d, J = 8.78 Hz, 4H), 8.2−8.14 (m, 3H), 8.2−8.36 (m, 4H), 8.94 (bs, 1H), 9.03 (bs, 1H), 9.12 (bs, 2H), 9.19 (bs, 2H). ^{13}C NMR (125 MHz, 80 °C, DMSO) δ 106.9, 106.9, 107.2, 107.3, 107.3, 110.6, 111.2, 112.2, 113.0, 114.1, 118.1, 118.4, 118.4, 118.5, 118.6, 120.8, 120.9, 126.9, 127.0, 127.2, 127.3, 127.7, 128.9, 129.1, 129.2, 134.3, 137.9, 139.3, 139.7, 139.8, 140.0, 140.0, 140.3, 140.4, 140.5, 140.6, 163.9, 164.1, 164.1. IR (neat) ν 3404, 3289, 1582, 1494, 1410 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 278 (2.6). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3648.

*N,N′-Bis[4,6-bis(2-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-o-phenylenediamine (**8c**).* From *N*-2-aminophenyl-*N*′,*N*″-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**5c**) (0.12 mmol, 0.06 g), 6-chloro-*N*,*N*′-bis(2-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1c**) (0.12 mmol, 0.051 g), DIPEA (0.12 mmol, 0.015 g), and DMSO (0.5 mL). White solid, 0.202 g (94%), mp 105−108 °C (decomp). ^{1}H NMR (300 MHz, 80 °C, DMSO) δ 6.49 (m, 4H), 7.17 (m, 6H), 7.27 (t, J = 7.14 Hz, 4H), 7.48 (d, J = 7.69 Hz, 4H), 7.66 (m, 2H), 7.78 (d, J = 1.76 Hz, 4H), 8.1 (d, J = 2.42 Hz, 4H), 8.17 (d, J = 7.88 Hz, 4H), 8.61 (bs, 2H), 9.33 (bs, 4H). ^{13}C NMR (75 MHz, 80 °C, DMSO) δ 106.5, 123.2, 123.3, 123.7, 124.0, 125.1, 126.9, 130.4, 130.5, 130.7, 131.1, 131.6, 140.4, 163.9, 164.4. IR (neat) ν 3283, 1574, 1505, 1446, 1414 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 245, 285 (1.98). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3658.

*N,N′-Bis[4,6-bis(3-pyrazol-1-ylphenylamino)-1,3,5-triazin-2-yl]-o-phenylenediamine (**8d**).* From *N*-2-aminophenyl-*N*′,*N*″-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4,6-triamine (**5d**) (0.16 mmol, 0.07 g), 6-chloro-*N*,*N*′-bis(3-pyrazol-1-ylphenyl)-1,3,5-triazine-2,4-diamine (**1d**) (0.16 mmol, 0.06 g), DIPEA (0.12 mmol, 0.015 g), and DMSO (0.5 mL). White solid, 0.127 g (94%), mp 108 °C (decomp). ^{1}H NMR (300 MHz, 80 °C, DMSO) δ 6.48 (t, J = 2.20 Hz, 4H), 7.1 (m, 2H), 7.27 (t, J = 8.02 Hz, 4H), 7.39 (d, J = 7.25 Hz, 4H), 7.68 (d, J = 1.76 Hz, 4H), 7.74 (pseudo d, J = 5.93 Hz, 6H), 8.06 (t, J = 1.98 Hz, 4H), 8.18 (d, J = 2.42 Hz, 4H), 8.49 (bs, 2H), 9.29 (bs, 4H). ^{13}C NMR (75 MHz, 80 °C, DMSO) δ 107.1, 110.6, 112.2, 118.0, 124.2, 124.4, 125.4, 127.1, 128.8, 131.8, 139.6, 140.2, 140.3, 140.4, 164.1, 164.5. IR (neat) ν 3379, 3290, 1582, 1504, 1400 cm^{-1}. UV λ_{max}/nm (ε/10^5 mol L^{-1} cm^{-1}) 263 (2.2). MS (FAB-B) m/z [M + H]$^+$ calcd for $C_{48}H_{39}N_{20}$ 895.3667, found 895.3654.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Dynamic behavior by NMR spectroscopy; determination of quantum yields; and NMR, UV−vis, fluorescence, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: Antonio.Hoz@uclm.es.

*E-mail: Ana.Smigallon@uclm.es.

Present Addresses

†A.R.-C.: Institute of Science and Supramolecular Engineering (ISIS), University of Strasbourg, 8 Allée Gaspard Monge, Strasbourg Cedex 67083, France.

‡O.N.: Facultad de estudios superiores Cuautitlán, Universidad Nacional Autónoma de México (UNAM), 54740 Cuautitlán Izcali, México.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the DGCYT of Spain through Project CTQ2011-22410/BQU is acknowledged.

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