Carbazole- and Triphenylamine-Substituted Pyrimidines
Synthesis and Photophysical Properties

Sylvain Achelle, Julián Rodríguez-López, Massinissa Larbani, Rodrigo Plaza-Pedroche, Françoise Robin-Le Guen

To cite this version:
Sylvain Achelle, Julián Rodríguez-López, Massinissa Larbani, Rodrigo Plaza-Pedroche, Françoise Robin-Le Guen. Carbazole- and Triphenylamine-Substituted Pyrimidines Synthesis and Photophysical Properties. Molecules, MDPI, 2019, 24 (9), 10.3390/molecules24091742. hal-02150442

HAL Id: hal-02150442
https://hal-univ-rennes1.archives-ouvertes.fr/hal-02150442
Submitted on 6 Apr 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Carbazole- and Triphenylamine-Substituted Pyrimidines: Synthesis and Photophysical Properties

Sylvain Achelle 1,*; Julián Rodríguez-López 2,*; Massinissa Larbani 1; Rodrigo Plaza-Pedroche 2 and Françoise Robin-le Guen 1

1 Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes-UMR 6226, F 35000 Rennes, France; massilarb06@gmail.com (M.L.); francoise.le-guen@univ-rennes1.fr (F.R.-l.G.)
2 Área de Química Orgánica, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La-Mancha, Avda. Camilo José Cela 10, 13071 Ciudad Real, Spain; rodripedroche@gmail.com
* Correspondence: sylvain.achelle@univ-rennes1.fr (S.A.); julian.rodriguez@uclm.es (J.R.-L.);
Tel.: +33-296-469-448 (S.A.); +34-926-295-300 (J.R.-L.)

Academic Editor: Frédéric Paul
Received: 11 April 2019; Accepted: 3 May 2019; Published: 5 May 2019

Abstract: A series of pyrimidine derivatives bearing one, two or three triphenylamine/9-ethylcarbazole substituents has been synthesized by Suzuki cross-coupling reaction. All compounds showed absorption bands in the UV region and the emission of violet-blue light upon irradiation. Protonation led to quenching of the fluorescence, although some derivatives remained luminescent with the appearance of a new red-shifted band in the spectra. Accurate control of the amount of acid enabled white photoluminescence to be obtained both in solution and in solid state.

Keywords: pyrimidines; fluorescence; white-light emission; intramolecular charge transfer

1. Introduction

The pyrimidine (1,3-diazine) core is a π-deficient six-membered heterocycle with two nitrogen atoms. Consequently, the pyrimidin-4-yl and the pyrimidin-2-yl fragments act as relatively strong electron-withdrawing groups [1]. With regard to pyridyl analogues, the presence of an appropriately positioned second nitrogen atom significantly enhances their electron-attracting character [2]. The pyrimidine ring has therefore been extensively used as an acceptor unit in push-pull structures in which significant intramolecular charge transfer (ICT) occurs [1,3,4]. In this respect, 4,6-di(arylvinyl)pyrimidines are now well established two-photon absorption chromophores for biological imaging [5–8], 3D lithographic microfabrication [9], and 3D data storage [10]. Appropriately substituted 2,4,6-triarylpyrimidines have also been developed as efficient emitters for OLEDs due to their thermally activated delayed fluorescence (TADF) properties [11–15]. Pyrimidine push-pull chromophores have also been developed as second order nonlinear optic (NLO) materials [16,17] and as dyes for photovoltaic applications [18,19].

When compared to their arylvinyl- and arylethynyl- analogues, arylpyrimidines generally exhibit a blue-shifted emission with a higher emission quantum yield [1,20]. Arylpyrimidines can be easily obtained by Suzuki cross-coupling reaction from halogenopyrimidines [21–24]. The electron-withdrawing character of the pyrimidinyl fragments allows this reaction to be performed from chloro-derivatives [25].

The emission properties of pyrimidine fluorophores are highly sensitive to the environment. As a consequence, a strong emission solvatochromism, which is typical of ICT chromophores [26–29], is observed: a polarity increase provides a significant bathochromic shift of the emission band [30–33]. On the other hand, protonation of the pyrimidine ring (pK_a = 1.1) significantly enhances its electron-withdrawing character and leads to a red-shift of both absorption and emission bands. These shifts are generally accompanied by emission quenching, but in some cases, particularly with weak electron-donating groups...
such as methoxy fragments, red-shifted emission with increased intensity is observed [32,34,35]. White photoluminescence can be obtained both in solution and in doped polystyrene films when the neutral and protonated forms are present in the appropriate ratio [34,35].

Triphenylamine and 9-ethylcarbazole have been extensively used as electron-donating units in push-pull structures [36–39]. Although these units are weaker electron donors than \( N,N \)-dialkylanilines [40], derivatives that incorporate these moieties generally have stronger luminescence properties [41–43]. Nevertheless, only a few pyrimidine derivatives bearing triphenylamine or 9-ethylcarbazole fragments have been described in the literature [9,19,44,45].

We report here the synthesis of a series of pyrimidine chromophores with one, two or three triphenylamine/9-ethylcarbazole substituents. The photophysical properties of the new materials were carefully studied and the luminescence behaviour in the presence of acid was evaluated. In some cases, the protonated pyrimidines remained emissive, which enabled white luminescence to be obtained by accurate control of the amount of acid.

2. Results and Discussion

2.1. Synthesis

Compounds 1 and 2 were obtained in moderate to good yield by Suzuki cross-coupling reaction from the corresponding chloropyrimidines and boronic acids according to a known methodology for similar pyrimidine structures (Scheme 1) [21–24]. All compounds were identified by \(^1\)H and \(^{13}\)C-NMR, and all previously unknown molecules were also characterized by high resolution mass spectroscopy (HRMS).

\[
\text{Scheme 1. Preparation of pyrimidines 1 and 2. (i) Toluene, Pd(PPh}_3)_4, \text{Na}_2\text{CO}_3 \text{aq., EtOH, } \Delta, 15 \text{ h.}}
\]
2.2. Photophysical Properties in Solution

The UV-Vis and photoluminescence (PL) spectroscopic data for compounds 1 and 2 in dichloromethane are presented in Table 1. The analyses were carried out using low concentration solutions (1.0–2.0 × 10⁻⁵ M). Self-absorption effects were not observed under the conditions employed. As representative examples, the spectra of compounds 1a–c are shown in Figure 1 (see Figure S1 in the Supporting Information for spectra of compounds 2a–c).

Table 1. UV-Vis and photoluminescence (PL) data for compounds 1 and 2 in CH₂Cl₂ solution.

| Compd | λₐₛₛ (nm) | ε (mM⁻¹ cm⁻¹) | λₐₑ (nm) | Φ_F | Stokes Shift (cm⁻¹) |
|-------|------------|----------------|----------|-----|--------------------|
| 1a    | 356, 301   | 21.7, 13.3     | 456      | 0.83| 6160               |
| 1b    | 388, 301   | 52.0, 26.4     | 486      | 0.86| 5200               |
| 1c    | 376, 299, 293 | 76.6, 36.7, 36.9 | 475  | 0.52| 5540               |
| 2a    | 323, 284, 276 (sh) | 22.6, 51.6, 33.8 | 382  | 0.32| 4780               |
| 2b    | 360, 348, 284 | 43.2, 48.2, 50.1 | 407  | 0.77| 3210               |
| 2c    | 367 (sh) 339, 299, 282 (sh) | 20.4, 69.2, 84.2, 64.1 | 398  | 0.35| 2120               |

Figure 1. Normalized absorption (dashed lines) and emission (solid lines) spectra of compounds 1a (green), 1b (blue) and 1c (red) in dichloromethane solution.

Compounds 1, which contain triphenylamine substituents, exhibited red-shifted absorption and emission bands with respect to their 9-ethylcarbazole analogues 2. This finding indicates that the 9-ethyl-9H-carbazol-3-yl fragment is a weaker electron-donating group than triphenylamine. Triphenylamine derivatives 1 also displayed higher fluorescence quantum yields (up to 0.86 for 1b). The 4,6-disubstituted pyrimidines 1b and 2b showed a red-shifted emission and an enhanced fluorescence quantum yield in comparison with their C2-mono-substituted analogues 1a and 2a. In contrast, the addition of a third substituent (2,4,6-triarylpymidinides) led to a slight blue shift in the emission and a decrease in the quantum yield. A similar phenomenon has previously been observed in tristyrylpyrimidines and was attributed to a decrease in the electron-withdrawing character of the pyrimidine central core due to the C2 electron-donating substituent, which decreases the ICT along the C4 and C6 arms [32].

In an effort to gain further insights into the photophysical properties of these push-pull molecules, in particular to evaluate the ICT upon excitation, the emission behaviour of compounds 1 and 2 was studied in a variety of different aprotic solvents. The data obtained are summarized in Table 2. The position of the longest wavelength absorption maximum was not affected significantly but an increase in the solvent polarity, estimated by the Dimroth–Reichardt polarity parameters [46,47].
resulted in a red-shifted emission (see Figure 2 for compound 1b and Figures S2–S6 in the Supporting Information for compounds 1a, 1c, and 2a–c). This bathochromic shift in the emission band is consistent with stabilization of the highly polar emitting excited state by polar solvents. The solvatochromic shift of the emission band can be used to evaluate the ICT upon excitation. For all compounds, the emission maxima were plotted versus the Dimroth–Reichardt polarity parameter, and in all cases good linearity was found (see Figure S7 in the Supporting Information). The slopes of the corresponding regression lines indicate a stronger ICT for triphenylamine derivatives 1 with respect to their 9-ethylcarbazole analogues 2. In the triphenylamine series, the slope increased in the order 1a < 1c < 1b, thus indicating that the strongest ICT was obtained for the 4,6-disubstituted pyrimidine 1b. In a similar way, the slope increased in the order 2a < 2c < 2b for the 9-ethylcarbazole derivatives.

Table 2. Emission solvatochromism of compounds 1 and 2 in various aprotic solvents.

| Compd | n-Heptane | Toluene | 1,4-Dioxane | THF | CHCl3 | CH2Cl2 | Acetone | MeCN |
|-------|-----------|---------|-------------|-----|-------|--------|---------|------|
| 1a    | 406       | 420     | 429         | 449 | 450   |        |         |      |
| 1b    | 418       | 437     | 444         | 464 | 478   | 486    | 498     | 518  |
| 1c    | 413       | 432     | 438         | 466 | 466   | 475    | 492     | 508  |
| 2a    | 354/373   | 361/378 | 362/379     | 379 | 383   | 382    | 382     | 389  |
| 2b    | 371       | 383     | 384         | 385 | 398   | 398    | 407     | 413  |
| 2c    | 379       | 384     | 386         | 385 | 398   | 398    | 407     | 415  |

| Compd | n-Heptane | Toluene | 1,4-Dioxane | THF | CHCl3 | CH2Cl2 | Acetone | MeCN |
|-------|-----------|---------|-------------|-----|-------|--------|---------|------|
| 1a    | 406       | 420     | 429         | 449 | 450   |        |         |      |
| 1b    | 418       | 437     | 444         | 464 | 478   | 486    | 498     | 518  |
| 1c    | 413       | 432     | 438         | 466 | 466   | 475    | 492     | 508  |
| 2a    | 354/373   | 361/378 | 362/379     | 379 | 383   | 382    | 382     | 389  |
| 2b    | 371       | 383     | 384         | 385 | 398   | 398    | 407     | 413  |
| 2c    | 379       | 384     | 386         | 385 | 398   | 398    | 407     | 415  |

* ET(30) Dimroth–Reichardt polarity parameter in kcal mol⁻¹.

![Figure 2. Normalized emission spectra of 1b in different aprotic solvents.](image)

Photophysical measurements were also performed on a 10⁻² M solution of camphorsulfonic acid (CSA) in dichloromethane. The results are summarized in Table 3. As one would expect, a bathochromic shift of the charge transfer absorption band was observed for all compounds due to the protonation of the pyrimidine ring [45,48]. This was associated with a dramatic quenching of the fluorescence for the triphenylamine derivatives. As a consequence, emission bands could not be identified for compounds 1a and 1c, whereas for 1b a low intensity emission in the red region was detected (λmax = 651 nm, ΦF < 0.01). It is worth noting that the protonated form of 1b was more emissive in chloroform solution (λabs = 493 nm, λem = 625 nm, ΦF = 0.11). In contrast, the 9-ethylcarbazole derivatives 2b and 2c remained fluorescent and they emitted green-yellow light with high emission quantum yields (ΦF = 0.63 and 0.45, respectively). The decay lifetimes (τ) were determined to be 3.6 ns and 4.2 ns (τ values for the neutral molecules were 1.8 ns and 1.7 ns, respectively). Surprisingly, 2a was not emissive in acidified dichloromethane. The effect of protonation was studied in a more detailed way by titration of solutions of compounds 1b, 2b and 2c with CSA. The changes observed in the UV-vis and emission spectra for 2b are illustrated in Figures 3 and 4, respectively (see the Supporting Information for data...
for compounds 1b and 2c). The absorption spectra showed the progressive disappearance of the charge transfer absorption band of the neutral form, whereas a red-shifted charge transfer absorption band for the protonated form progressively appeared. The presence of an isosbestic point is evident and this is characteristic of an equilibrium between two species (Figure 3). The same trend was observed in the emission spectra; the addition of CSA led to the progressive disappearance of the emission band of the neutral form and this was associated with the enhancement of a new red-shifted band corresponding to the emission of the protonated form with an isoemissive point (Figure 4).

### Table 3. UV/Vis and PL data for compounds 1 and 2 in acid solution (10−2 M CSA in CH2Cl2).

| Compd | λ_{abs} (nm) | ε (mM cm⁻¹) | λ_{em} (nm) | Φ | Stokes Shift (cm⁻¹) |
|-------|---------------|-------------|-------------|---|-------------------|
| 1a    | 424, 373 (sh), 268 | 17.2, 9.3, 30.5 | -          | - | -                |
| 1b    | 488          | 48.3        | 651         | <0.01 | 5130             |
| 1c    | 486, 375, 274 | 68.2, 30.4, 88.5 | -          | - | -                |
| 2a    | 396          | 27.3        | -           | - | -                |
| 2b    | 444, 390, 285 | 63.9, 28.0, 64.3 | 519        | 0.63 | 3250             |
| 2c    | 443, 330     | 41.9, 29.0  | 552         | 0.45 | 4460             |

**Figure 3.** Changes in the absorption spectra of a dichloromethane solution of 2b (c = 1.87 × 10⁻⁵ M) upon addition of CSA (0–20 equivalents).

**Figure 4.** Changes in the emission spectra of a dichloromethane solution of 2b (c = 1.97 × 10⁻⁵ M) upon addition of CSA (0–40 equivalents), λ_{exc} = 370 nm.
The coexistence of both neutral and protonated species with complementary emitting colors in the solution enabled white light emission to be achieved under UV-irradiation. Thus, compound 2c emitted violet light at $\lambda_{\text{max}} = 398$ nm and this turned to green-yellow at $\lambda_{\text{max}} = 552$ nm upon protonation. Excitation at 370 nm led to the observation of white light after the addition of 45 equivalents of CSA to a $1.25 \times 10^{-5}$ M solution of 2c in dichloromethane (Figure 5). The same phenomenon was also observed for compounds 1b and 2b (Figures S11 and S12 of the Supporting Information, respectively). For 1b and 2c, the calculated CIE chromaticity coordinates (Table 4) were close to those of pure white light (0.33, 0.33).

![Figure 5](image_url)

**Figure 5.** Changes in the color of a dichloromethane solution of 2c ($c = 1.25 \times 10^{-5}$ M) after the addition of 45 equivalents (middle) and in $10^{-5}$ M CSA (right). Photographs were taken in the dark upon irradiation with a hand-held UV lamp ($\lambda_{\text{em}} = 366$ nm).

| Compd | Neutral Form | Protonated Form | Mixture of Neutral and Protonated Forms |
|-------|--------------|-----------------|---------------------------------------|
| 1a $^d$ | (0.15, 0.15) | -               | -                                     |
| 1b $^b$ | (0.18, 0.33) | (0.62, 0.37)   | (0.32, 0.34) $^c$                     |
| 1c $^e$ | (0.16, 0.25) | -               | -                                     |
| 2a $^d$ | (0.18, 0.04) | -               | -                                     |
| 2b $^d$ | (0.16, 0.03) | (0.29, 0.59)   | (0.24, 0.39) $^d$                    |
| 2c $^d$ | (0.17, 0.04) | (0.42, 0.56)   | (0.30, 0.34) $^e$                    |

$^a$ In dichloromethane solution ($c = 1.0-2.0 \times 10^{-5}$ M). $^b$ In chloroform solution ($c = 9.76 \times 10^{-6}$ M). $^c$ 50 equivalents of CSA, $\lambda_{\text{exc}} = 400$ nm. $^d$ 2 equivalents of CSA, $\lambda_{\text{exc}} = 370$ nm. $^e$ 45 equivalents of CSA, $\lambda_{\text{exc}} = 370$ nm.

2.3. Photophysical Properties in Solid State

Filter paper pieces covered with 2b and 2c in the absence and presence of different amounts of CSA were prepared by immersion of the filter paper into a dichloromethane solution of the appropriate compound (1 wt% doped on polystyrene). The samples were dried in air. The fluorescence spectra of the samples were acquired and emission maxima in the violet region at $\lambda_{\text{max}} = 405$ nm and 406 nm, respectively, were determined in the absence of acid. The intensities of these bands gradually decreased on increasing the amount of CSA, whereas a distinctly novel enhanced emission appeared in the green-yellow region ($\lambda_{\text{max}} = 544$ nm for 2b and $\lambda_{\text{max}} = 554$ nm for 2c). After careful tuning of the number of equivalents of CSA, white light was observed due to the simultaneous emission from both the neutral and protonated compounds. These significant emission changes were easily followed by the naked eye under UV irradiation (Figure 6 and Figure S13 in the Supporting Information). Energy transfer between neutral and protonated molecules has been suggested for related systems [49].
A stirred mixture of the chloropyrimidine derivative (1 mmol), arylboronic acid (1.2 mmol per chlorine atom), Pd(PPh$_3$)$_4$ (0.05 mmol per chlorine atom), 1 M aqueous sodium carbonate (1.2 mmol, 1.2 mL per chlorine atom), and ethanol (1.5 mL) in degassed toluene (15 mL) was heated at reflux under nitrogen for 15 h in a Schlenk tube. The reaction mixture was cooled, filtered, and dissolved with a mixture of AcOEt and water 1:1 (50 mL) and the organic layer was separated. The aqueous layer was extracted with AcOEt (2 × 25 mL). The combined organic extracts were dried with MgSO$_4$ and the solvents were evaporated.
2-(4-Diphenylaminophenyl)pyrimidine (1a). The title compound was obtained according to the general procedure and purified by column chromatography (SiO₂, AcOEt/petroleum ether, 3:7). Beige solid. Yield: 87% (238 mg). Mp: 136–137 °C (lit.: 176–177 °C [50]). ¹H-NMR (300 MHz, CDCl₃): δ 7.17–7.05 (m, 9H), 7.31–7.27 (m, 4H), 8.28 (d, 2H, J = 9.0 Hz), 8.74 (d, 2H, J = 4.8 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 118.2, 122.1, 123.6, 125.2, 129.2, 129.4, 130.9, 147.3, 150.3, 157.1, 164.5.

4,6-bis(4-Diphenylaminophenyl)pyrimidine (1b). The title compound was obtained according to the general procedure and purified by column chromatography (SiO₂, AcOEt/petroleum ether, 3:7). Yellow solid. Yield: 87% (492 mg). Mp: 230–231 °C. ¹H-NMR (300 MHz, CDCl₃): δ 7.17–7.07 (m, 16H), 7.33–7.27 (m, 8H), 7.93 (d, 1H, J = 1.2 Hz), 7.99 (d, 4H, J = 9.0 Hz), 9.17 (d, 1H, J = 1.2 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 110.9, 122.0, 123.9, 125.3, 128.1, 129.5, 129.9, 147.1, 150.4, 159.0, 163.7. HRMS (ESI/ASAP), m/z calculated for C₄₀H₃₄N₄ [M + H]⁺ 567.2543, found 567.2546.

2,4,6-tris(9-Ethyl-9H-carbazol-3-yl)pyrimidine (1c). The title compound was obtained according to the general procedure and purified by column chromatography (SiO₂, AcOEt/petroleum ether, 3:7). Yellow solid. Yield: 65% (526 mg). Mp: >260 °C. ¹H-NMR (300 MHz, CDCl₃): δ 7.11–7.06 (m, 6H), 7.18–7.15 (m, 18H), 7.32–7.27 (m, 12H), 7.78 (s, 1H), 8.11 (d, 4H, J = 8.7 Hz), 8.51 (d, 2H, J = 8.7 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 107.9, 122.2, 122.4, 123.3, 123.7, 124.7, 124.9, 125.2, 128.1, 129.3, 129.4, 130.8, 132.1, 147.2, 147.4, 149.9, 150.2, 163.7, 164.0 HRMS (ESI/ASAP), m/z calculated for C₅₈H₄₄N₅ [M + H]⁺ 810.3591, found 810.3591.

2-(9-Ethyl-9H-carbazol-3-yl)pyrimidine (2a). The title compound was obtained according to the general procedure and purified by column chromatography (SiO₂, AcOEt/petroleum ether, 3:7). Beige solid. Yield: 87% (238 mg). Mp: 136–137 °C. ¹H-NMR (300 MHz, CDCl₃): δ 1.47 (t, 3H, J = 7.2 Hz), 4.41 (q, 6H, J = 7.2 Hz), 7.14 (t, 1H, J = 4.8 Hz), 7.30–7.27 (m, 1H), 7.52–7.42 (m, 3H), 8.22 (d, 1H, J = 7.8 Hz), 8.61 (d, 1H, J = 7.8 Hz), 8.82 (d, 2H, J = 5.1 Hz), 9.22 (s, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 13.9, 37.7, 108.4, 108.7, 118.1, 119.5, 120.8, 121.0, 123.3, 123.5, 126.0, 126.2, 128.6, 140.6, 141.8, 157.2, 165.6. HRMS (ESI/ASAP), m/z calculated for C₁₈H₁₆N₃ [M + H]⁺ 274.1338, found 274.1343.

4,6-bis(9-Ethyl-9H-carbazol-3-yl)pyrimidine (2b). The title compound was obtained according to the general procedure and purified by column chromatography (SiO₂, AcOEt/petroleum ether, 1:1). Pale yellow solid. Yield: 76% (352 mg). Mp: 170–171 °C (lit.: 176–177 °C [45]). ¹H-NMR (300 MHz, CDCl₃): δ 1.45 (t, 6H, J = 6.9 Hz), 4.33 (q, 4H, J = 6.9 Hz), 7.53–7.30 (m, 8H), 8.32–8.24 (m, 5H), 8.99 (s, 2H), 9.36 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃): δ 13.8, 37.7, 108.6, 108.8, 111.5, 119.6, 119.7, 120.8, 123.2, 123.5, 124.9, 126.2, 127.9, 140.6, 141.6, 159.0, 164.8.

2,4,6-tris(9-Ethyl-9H-carbazol-3-yl)pyrimidine (2c). The title compound was obtained according to the general procedure and purified by column chromatography (SiO₂, AcOEt/petroleum ether, 3:7) followed by recrystallization from CH₂Cl₂/n-heptane. Pale yellow solid. Yield: 51% (530 mg). Mp: 176–177 °C. ¹H-NMR (300 MHz, CDCl₃): δ 1.52 (t, 9H, J = 6.3 Hz), 4.46 (q, 6H, J = 7.2 Hz), 7.37–7.33 (m, 3H), 7.62–7.47 (m, 9H), 8.22 (d, 1H, J = 2.4 Hz), 8.38–8.33 (m, 3H), 8.59 (2H, d, J = 8.7 Hz), 9.04 (1H, dd, J₁ = 8.7 Hz, J₂ = 1.2 Hz), 9.14 (s, 2H), 9.59 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃): δ 13.9, 37.8, 108.2, 108.7, 108.8, 119.2, 119.4, 119.8, 120.8, 120.9, 121.2, 123.2, 123.4, 123.5, 123.8, 125.4, 125.7, 126.1, 126.8, 129.1, 130.0, 140.6, 141.6. HRMS (ESI/ASAP), m/z calculated for C₄₆H₃₈N₅ [M + H]⁺ 660.3122, found 660.3122.

4. Conclusions

Push-pull pyrimidines substituted with a different number of either triphenylamine or 9-ethylcarbazole groups were prepared by Suzuki cross-coupling reaction from the corresponding chloropyrimidines and boronic acids. The molecules presented absorption wavelengths in the UV region and emitted violet-blue light in dichloromethane solution with a higher fluorescence quantum yield and a stronger ICT observed for the triphenylamine derivatives. The addition of acid was accompanied by a dramatic quenching of the fluorescence except for the 9-ethylcarbazole derivatives 2b and 2c (and partially for 1b). In these cases, protonation led to the progressive disappearance of the
emission band and the appearance of a new red-shifted complementary emitting band. Thus, white photoluminescence could be obtained by controlled protonation. White emission was also achieved in solid state.

Supplementary Materials: The following material is available online: Figure S1: absorption and emission spectra of compounds 2a–c in dichloromethane solution; Figures S2–S6: emission spectra of 1a, 1c, and 2a–c in different aprotic solvents; Figure S7: emission maxima as a function of the Dimroth–Reichardt polarity parameter E(30) for compounds 1 and 2; Figures S8–S10: changes in the absorption and emission spectra of a solution of 1b and 2b upon addition of CSA; Figures S11 and S12: changes in the color of a solution of 1b and 2b after the addition of CSA; Figure S13: fluorescence spectra and changes in the color of 2b in solid state after the addition of CSA; Figures S14–S23: 1H, 13C-NMR and HRMS spectra of compounds 1 and 2.

Author Contributions: Conceptualization, S.A. and J.R.-L.; Formal analysis, S.A. and J.R.-L.; Funding acquisition, J.R.-L. and F.R.-I.G.; Investigation, S.A., J.R.-L., M.L. and R.P.-P.; Supervision, S.A. and J.R.-L.; Writing—original draft, S.A.; Writing—review & editing, J.R.-L. and F.R.-I.G.

Funding: This research was funded by the Junta de Comunidades de Castilla-La Mancha/FEDER (project SBPLY/17/180501/000214) and the Ministerio de Economía y Competitividad/Agencia Estatal de Investigación/FEDER (project CTQ2017-84561-P).

Acknowledgments: Olivier Mongin, Institut des Sciences Chimiques de Rennes, is acknowledged for helpful discussions.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Achelle, S.; Rodríguez-López, J.; Robin-le Guen, F. Photoluminescence properties of aryl-arylvinyl- and arylethenylpyrimidine derivatives. *ChemistrySelect* 2018, 3, 1852–1885. [CrossRef]
2. Aranda, A.I.; Achelle, S.; Hammerer, F.; Mahuteau-Betzer, F.; Teulade-Fichou, M.-P. Vinyl-diazine triphenylamines and their N-methylated derivatives: synthesis, photophysical properties and application for staining DNA. *Dyes Pigm.* 2012, 95, 400–407. [CrossRef]
3. Lipunova, G.N.; Nosova, E.V.; Charushin, V.N.; Chupakhin, O.N. Functionalized quinazolines and pyrimidines for optoelectronics. *Curr. Org. Synth.* 2018, 15, 793–814. [CrossRef]
4. Achelle, S.; Plé, N. Pyrimidine ring as building block for the synthesis of functionalized π-conjugated materials. *Curr. Org. Synth.* 2012, 9, 163–187. [CrossRef]
5. Li, L.; Ge, J.; Wu, H.; Xu, Q.-H.; Yao, S.Q. Organelle-specific detection of phosphatase activities with two-photon fluorogenic probes in cells and tissues. *J. Am. Chem. Soc.* 2012, 134, 12157–12167. [CrossRef] [PubMed]
6. Na, Z.; Li, L.; Uttamchandani, M.; Yao, S.Q. Microarray-guided discovery of two-photon (2P) small molecule probes for live-cell imaging of cysteinyl cathepsin activities. *Chem. Commun.* 2012, 48, 7304–7306. [CrossRef] [PubMed]
7. Zhang, Q.; Tian, X.; Hu, Z.; Brommessen, C.; Wu, J.; Zhou, H.; Yang, J.; Sun, Z.; Tian, Y.; Uvdal, K. Nonlinear optical response and two-photon biological applications of a new family of imidazole-pyrimidine derivatives. *Dyes Pigm.* 2016, 126, 286–295. [CrossRef]
8. Liu, B.; Zhang, H.-L.; Liu, J.; Zhao, Y.-D.; Luo, Q.-M.; Huang, Z.-L. Novel pyrimidine-based amphiphilic molecules: synthesis, spectroscopic properties and applications in two-photon fluorescence imaging. *J. Mater. Chem. C* 2017, 16, 2921–2929. [CrossRef]
9. Malval, J.-P.; Achelle, S.; Bodiou, L.; Spangenberg, A.; Gomez, L.C.; Soppera, O.; Robin-le Guen, F. Two-photon absorption in a conformationally twisted D–π-A oligomer: a synergic photosensitizing approach for multiphoton lithography. *J. Mater. Chem. C* 2014, 4, 7869–7880. [CrossRef]
10. Li, L.; Tian, Y.; Yang, J.-X.; Sun, P.-P.; Wu, J.-Y.; Zhou, H.-P.; Zhang, S.-Y.; Jin, B.-K.; Xing, X.-J.; Wang, C.-K.; et al. Facile synthesis and systematic investigations of a series of novel bent-shaped two-photon absorption chromophores based on pyrimidine. *Chem. Asian J.* 2009, 4, 668–680. [CrossRef]
11. Serevičius, T.; Bučiūnas, T.; Bučevičius, J.; Dodonova, J.; Tumkevičius, S.; Kazlauskas, K.; Juršėnas, S. Room-temperature phosphorescence vs. thermally activated delayed fluorescence in cabazole pyrimidine cored compounds. *J. Mater. Chem. C* 2018, 6, 11128–11136. [CrossRef]
12. Li, B.; Li, Z.; Hu, T.; Zhang, Y.; Wang, Y.; Yi, Y.; Guo, F.; Zhao, L. Highly efficient blue organic light-emitting diodes from pyrimidine-based thermally activated delayed fluorescence emitters. J. Mater. Chem. C 2018, 6, 2351–2359. [CrossRef]

13. Komatsu, R.; Sasabe, H.; Kido, J. Recent progress of pyrimidine derivatives for high-performance organic light-emitting devices. J. Photonics Energy 2018, 8, 032108. [CrossRef]

14. Komatsu, R.; Ohsawa, T.; Sasabe, H.; Nakao, K.; Hayasaka, Y.; Kido, J. Manipulating the electronic excited state energies of pyrimidine-based thermally activated delayed fluorescence emitters to realize efficient deep-blue emission. ACS Appl. Mater. Interfaces 2017, 9, 4742–4749. [CrossRef] [PubMed]

15. Nakao, K.; Sasabe, H.; Komatsu, R.; Hayasaka, Y.; Ohsawa, T.; Kido, J. Unlocking the potential of pyrimidine conjugate emitters to realize high-performance organic light-emitting devices. Adv. Opt. Mater. 2017, 5, 1600843. [CrossRef]

16. Durand, R.J.; Gauthier, S.; Achelle, S.; Groizard, T.; Kahlal, S.; Saillard, J.-Y.; Barsella, A.; le Poul, P.; Robin-le Guen, F. Push-pull D-π-Ru-π-A chromophores: synthesis and electrochemical, photophysical and second-order nonlinear optical properties. Dalton Trans. 2018, 47, 3965–3975. [CrossRef] [PubMed]

17. Achelle, S.; Kahlal, S.; Barsella, A.; Saillard, J.-Y.; Che, X.; Vallet, J.; Bureš, F.; Caro, B.; Robin-le Guen, F. Improvement of the quadratic non-linear optical properties of pyrimidine chromophores by N-methylation and tungsten pentacarbonyl complexation. Dyes Pigm. 2015, 113, 562–570. [CrossRef]

18. Sun, H.; Liu, D.; Wang, T.; Li, P.; Bridgmohan, C.N.; Li, W.; Lu, T.; Hu, W.; Wang, L.; Zhou, X. Charge-separated sensitizers with enhanced intramolecular charge transfer for dye-sensitized solar cells: Insight from structure-performance relationships. Org. Electron. 2018, 61, 35–45. [CrossRef]

19. Verbitskiiy, E.V.; Cheprakova, E.M.; Subbotina, J.O.; Schepochkin, A.V.; Slepukhin, P.A.; Rusinov, G.L.; Charushin, V.N.; Chupakhin, O.N.; Makarova, N.I.; Metelitsa, A.V.; et al. Synthesis, spectral and electrochemical properties of pyrimidine-containing dyes as photosensitizers for dye-sensitized solar cells. Dyes Pigm. 2014, 100, 201–204. [CrossRef]

20. Achelle, S.; Robin-le Guen, F. Emission properties of diazone chromophores: structure-properties relationship. J. Photochem. Photobiol. A 2017, 348, 281–286. [CrossRef]

21. Schomaker, J.M.; Delia, T.J. Arylation of halogenated pyrimidines via a Suzuki coupling reaction. J. Org. Chem. 2001, 66, 7125–7128. [CrossRef] [PubMed]

22. Anderson, S.C.; Handy, S.T. One-pot double Suzuki couplings of dichloropyrimidines. Synthesis 2010, 2721–2724.

23. Delia, T.J.; Schomaker, J.M.; Kalinda, A.S. The synthesis of substituted phenylpyrimidines via Suzuki coupling reactions. J. Heterocycl. Chem. 2006, 43, 127–131. [CrossRef]

24. Achelle, S.; Ramondenc, Y.; Marsais, F.; Plé, N. Star- and banana-shaped oligomers with a pyrimidine core: synthesis and light-emitting properties. Eur. J. Org. Chem. 2008, 3129–3140. [CrossRef]

25. Littke, A.F.; Höwedes, S.P.; Gers-Panther, C.F.; Gruber, I.; Janiak, C.; Müller, T.J.J. Palladium-catalyzed coupling reactions of aryl chlorides. J. Org. Chem. 2002, 67, 4176–4179. [CrossRef]

26. Lartia, R.; Allain, C.; Bordeau, G.; Schmidt, F.; Fiorini-Debuisschert, C.; Charra, F.; Teulade-Fichou, M.-P. Synthetic strategies to derivatizable triphenylamine displaying high two-photon absorption. J. Org. Chem. 2006, 73, 1732–1744. [CrossRef]

27. Littke, A.F.; Fu, G.C. Synthetic strategies to derivatizable triphenylamine displaying high two-photon absorption. J. Org. Chem. 2008, 73, 1732–1744. [CrossRef]

28. Katan, C.; Charlot, M.; Mengin, O.; Le Droumaguet, C.; Jouikov, V.; Terenziani, F.; Badaeva, E.; Tretiak, S.; Blanchard-Desce, M. Synthetic strategies to derivatizable triphenylamine displaying high two-photon absorption. J. Org. Chem. 2008, 73, 1732–1744. [CrossRef]

29. Merkt, F.K.; Höwedes, S.P.; Gers-Panther, C.F.; Gruber, I.; Janiak, C.; Müller, T.J.J. Three-component activation/alkynylation/cyclocondensation (AACC) synthesis of enhanced emission solvatochromic π-A chromophores: synthesis and electrochemical, photophysical and second-order nonlinear optical properties. J. Phys. Chem. A 2010, 114, 3152–3169. [CrossRef]

30. Muraoka, H.; Obara, T.; Ogawa, S. Systematic synthesis, comparative studies of the optical properties, and the ICT-based sensor properties of a series of 2,4,6-tri(5-aryl-2-thienyl)pyrimidines with the D-π-A system. Tetrahedron Lett. 2016, 57, 3011–3015. [CrossRef]
Sample Availability: Samples of the compounds 1 and 2 are available from the authors.