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Improvement of the quadratic non-linear optical properties of pyrimidine chromophores by N-methylation and tungsten pentacarbonyl complexation

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4 Improvement of the quadratic non-linear optical
5 properties of pyrimidine chromophores by *N*-
6 methylation and tungsten pentacarbonyl
7 complexation.
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4 **Abstract**
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6 In this contribution, we report the synthesis of two series of compounds: 4-(arylviny)-1-
7 methylpyrimidinium derivatives and tungsten pentacarbonyl complexes of 4-
8 (arylviny)pyrimidines. Their second order non-linear properties, measured by Electric-Field
9 Induced Second Harmonic generation (EFISH) method, and their photophysical behavior
10 were thoroughly investigated and compared to the corresponding 4-(arylviny)pyrimidines. A
11 strong enhancement of the NLO response was observed upon methylation or complexation by
12 $W(CO)_5$ of the pyrimidine ring. DFT theoretical calculations were performed to provide
13 complementary insights on the structure-properties relationships in particular concerning the
14 amplitude of the NLO response.
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26 **Key words:** Pyrimidine, Internal Charge Transfer, Push-Pull chromophores, Tungsten
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28 Pentacarbonyl Complexes, Non-linear Optics, Theoretical calculations
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34 **1. Introduction**
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36 Compounds with second-order nonlinear optical (NLO) properties are important as
37 molecular building block materials for optical communications, optical data processing and
38 storage or electro-optical devices [1]. The most widely studied second order (quadratic) NLO
39 effects such as second harmonic generation (SHG) arise from high first molecular
40 hyperpolarizabilities β . The typical design of molecules presenting large β values consists in
41 dipolar molecules (D- π -A) also called push-pull. The D- π -A molecules possess an electron-
42 donating (D) and an electron-withdrawing (A) groups linked through a π -conjugated spacer
43 which provides the molecule an internal charge transfer (ICT) upon excitation.
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55 Pyrimidine, which is a highly π -deficient aromatic heterocycle, can therefore be used as
56 electron withdrawing part in push-pull molecules [2]. Moreover, the ICT along the molecule
57 backbone can also induce luminescence properties. The ability of protonation, hydrogen bond
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4 formation and chelation of the nitrogen atoms of the pyrimidine ring are also of great
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6 importance and, therefore, such derivatives could be used for the formation of supramolecular
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8 assemblies and as sensors. The pyrimidine ring was also largely used in the structure of two-
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10 photon absorption (TPA) chromophores and 4,6-di(arylvinyl)pyrimidines have become a
11
12 well-established TPA chromophore design [3]. Some quadratic NLO chromophores
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14 incorporating pyrimidine fragment were also described [4]. During the past decade, some of
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16 us have described a large library of pyrimidine derivatives presenting ICT [5]. In particular
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18 we have described the synthesis and the quadratic NLO response of a series of 4-
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20 (arylvinyl)pyrimidines [6]. Recently, the NLO properties of the same compounds have been
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22 subjected to theoretical investigation by another team [7].
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27 Two design strategies have been described for increasing the second-order NLO
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29 polarizability of push-pull molecules [8]. The first one consists in the elongation of the
30
31 conjugation pathway. The second one consists in increasing the strength of the donor and/or
32
33 the acceptor. In this context, using the nitrogen lone electron pair of electron-withdrawing
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35 azaheterocycle, either by protonation, *N*-alkylation/*N*-arylation or complexation, is an
36
37 interesting strategy. We have already demonstrated that the protonation of the nitrogen atoms
38
39 of pyrimidine push-pull derivatives lead to an increased ICT as shown by the bathochromic
40
41 shifts observed in UV-vis spectra [5c, 5e,f, 6]. Recently, Cariati and coworkers described
42
43 pH-triggered pyridine based NLO switch [9]. *N*-Alkylation and *N*-arylation were efficiently
44
45 applied on pyridine and benzothiazole derivatives in particular by the working groups of
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47 Clays and Vaquero [10]. Finally, another way to increase the electron attracting strength of
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49 azaheterocycles consists in complexation of their nitrogen lone electron pair by a transition
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51 metal and some metal carbonyl based NLO chromophores have already been described [11].
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53 To the best of our knowledge, none of these strategies have been tested on pyrimidine NLO
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55 chromophores.
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4 As a continuation of our research interest in the synthesis of heterocyclic second-order
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6 NLO chromophores [4b, 6, 12], we focus herein on exploration of *N*-methylated
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8 pyrimidinium and tungsten pentacarbonyl pyrimidine complex and to compare their second-
9
10 order NLO response with previously described pyrimidine derivatives. Experimental data are
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12 supported by DFT/TD-DFT theoretical analysis.
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18 **2. Results and Discussion**

19 *2.1. Synthesis*

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21 Starting from already described 4-(arylvinyl)pyrimidines **1-4** [6], tungsten pentacarbonyl
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23 complexes **5-8** were obtained according to the procedure described on pyridine derivatives
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25 [13] (Scheme 1). The complexation reaction is regiospecific, probably due to steric reasons
26
27 and the new complexes **5-8** were obtained in good yields.
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32 <Scheme 1>

33
34 The *N*-methylation of compounds **2** and **4** was carried out with iodomethane at reflux without
35
36 solvent. As described in the literature [14], *N*-methylation occurs regioselectively on the
37
38 diazine rings and methylated derivatives **9** and **10** were obtained in good yields (Scheme 2). It
39
40 should be noted that this strategy is not applicable on dimethylamino derivatives **1** and **3**:
41
42 methylation of the amino group is observed in addition to the methylation of the pyrimidine
43
44 ring. A reversal strategy in which the methylation step was carried out before the
45
46 condensation has been tested. However when using similar conditions, the methylation of 4-
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48 methylpyrimidine is not regioselective and led to a mixture of 1,4-dimethyl-pyrimidin-1-ium
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50 and 3,4-dimethyl-pyrimidin-3-ium in 8/2 ratio.
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55 <Scheme 2>

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57 All new compounds are soluble in THF, chloroform and dichloromethane and were
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59 characterized using a variety of analytical techniques. NMR experiments proved very useful
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4 to confirm the structures of the compounds (see Experimental Section and Supporting
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6 Information). The stereochemistry of the double bonds was unequivocally established on the
7
8 basis of the coupling constant for the vinylic protons in the ^1H NMR spectra ($J \approx 16$ Hz).
9
10 These materials are perfectly stable in the solid state and could be stored without the need for
11
12 special precautions.
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14 15 *2.2. Linear optical properties*

16
17 The UV-Vis and photoluminescence (PL) spectroscopic data of compound **1-10** measured in
18
19 dichloromethane at 25°C are presented in table 3. Analyses have been carried out using low
20
21 concentration solutions (1.0×10^{-5} to 3.0×10^{-5} M for UV/Vis spectra and 1.0×10^{-6} to $3.0 \times$
22
23 10^{-6} M for PL spectra). Under these conditions, self-absorption effects were not observed. All
24
25 compounds are photostable and did not undergo *cis-trans* isomerization under the analysis
26
27 conditions. As an example, the absorption spectra for derivatives **2**, **6** and **9** are shown in
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29 Figure 1.
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36 <Figure 1>

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38 As expected the complexation and more importantly the methylation of chromophores **1-4** led
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40 to a red shift of their absorption band. Whereas compound **1-4** are fluorescent, tungsten
41
42 derivatives **5-8** and methylated compounds **9** and **10** are completely non-emissive.
43
44 Biphenylenevinylene derivatives exhibit blue shifted absorptions in comparison to their
45
46 phenylenevinylene analogues. On the other hand biphenylenevinylene derivatives **3** and **4** are
47
48 red-shifted in emission when compared to **1** and **2** respectively.
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51 In order to study the ionic character of methylpyrimidinium derivative **9**, an absorption
52
53 solvatochromic study was performed (Figure 2, Table 2). Pyrimidinium derivative **9** showed
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55 absorption maxima of about 500 nm in nonpolar *n*-heptane and dipolar/protic solvents such as
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57 acetonitrile, DMSO and methanol and the most bathochromically shifted CT-bands were
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4 observed in polarizable dichloromethane/chloroform (550 and 545 nm). This observation
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6 implies that the excited state can be effectively stabilized by polarizable halogenated solvents.
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8 These results are in contrast to standard behavior of D- π -A molecules [5c-f, 6] and can be
9
10 attributed to ionic structure of **9** [15]. The impact of the ionic structure of **9** can be further
11
12 demonstrated by the observed blue shift of the absorption band in CH₂Cl₂ solution with
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14 increasing its concentration indicating aggregation (Table 3). Similar behavior was observed
15
16 for compound **10** (Figure S69, Tables S70-S71)
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18

19
20 <Figure 2>

21
22 <Table 2>

23
24 <Table 3>

25 26 27 28 29 *2.3. Second order NLO properties*

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31 Second-order non-linear properties were studied in CHCl₃ solution using the electric-field-
32
33 induced second-harmonic generation technique (EFISH), which provides information about
34
35 the scalar product $\mu\beta(2\omega)$ of the vector component of the first hyperpolarisability tensor β
36
37 and the dipole moment vector [16]. This product is derived according to equation 1 and
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39 considering $\gamma_0(-2\omega, \omega, \omega, 0)$, the third-order term, as negligible for the push-pull compounds
40
41 under consideration. This approximation is usually used for push-pull organic and
42
43 organometallic molecules.
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$$47 \gamma_{\text{EFISH}} = \mu\beta/5kT + \gamma_0(-2\omega, \omega, \omega, 0)$$

48 49 50 **Equation 1**

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52 Measurements were performed at 1907 nm, obtained from a Raman-shifted Nd:YAG⁺ laser
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54 source, which allowed us to work in conditions far from the resonance peaks of the
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56 compounds we were investigating (**1-10**). It should be noted that the sign and values of $\mu\beta$
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58 depend on the “direction” of the transition implied in the NLO phenomena and on the
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4 direction of the ground-state dipole moment. When β and μ were parallel (antiparallel) and
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6 positive (negative), maximal $\mu\beta$ values were obtained.
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9 The $\mu\beta$ values of compounds **1-10**, (Table 4) are positive indicating excited states more
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11 polarized than the ground state ($\mu_e > \mu_g$). In addition, this implies that the ground and excited
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13 states are polarized in the same direction.
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16 <Table 4>
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18 The $\mu\beta$ values observed for compounds **1-4** are relatively high, and similar to or higher than
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20 Disperse Red 1, as reported in literature [17]. For compounds **1**, **2** and **4**, an increase of the
21
22 NLO response is observed after complexation (compounds **5**, **6** and **8**), however a similar
23
24 response was observed for uncomplexed and complexed pyrimidine **3** and **7**. The positive $\mu\beta$
25
26 values for **5-8** suggest that the pyrimidine ring serves as a primary acceptor and the amino
27
28 group as a donor. The $W(CO)_5$ fragment acts as an auxiliary acceptor and consequently the
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30 MLCT transition has a negligible impact on the NLO phenomena. Similar mechanism was
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32 proposed for $M(CO)_5$ pyridine complexes bearing donor groups[18]. The effect of
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34 methylation is higher: compound **9** exhibits a $\mu\beta$ value more than 12 times higher than
35
36 compound **2** and methylation of compound **4** results in a five-fold increase of the NLO
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38 response. The observed $\mu\beta$ for **9** is 2.8 higher than that of a corresponding iodopyridinium
39
40 compound of similar length, which is in accordance with the higher pyrimidinium acceptor
41
42 strength [19]. Whereas the $\mu\beta$ value clearly increases when going from phenylenevinylene
43
44 derivative **1** to biphenylenevinylene compound **3**, this trend is less perceptible in case of
45
46 diphenylamino derivatives **2** and **4** and an important decrease of the NLO response is
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48 observed with complexed and methylated molecules. When going from NMe_2 to NPh_2
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50 derivatives, a decrease of the NLO response is observed for pyrimidine compounds **1-2**, **3-4**.
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57 This trend is attenuated by the complexation (compounds **5-6**, **7-8**).
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4 <Figure 3>
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9 2.4. Computational studies

10 In order to get a better insight into the electronic structure of the title compounds, DFT
11 calculations have been performed on compounds **1-10**, as well as on the hypothetical
12 dimethylamino relatives of **9** and **10** which will be labeled **11** and **12** respectively, in the
13 following discussion. Their geometries were fully optimized with and without considering
14 solvent (CH₂Cl₂) effect corrections (see computational details) and little differences were
15 found between the vacuum and solvent-corrected geometries. Those of the diphenylamino
16 series are shown in Figure 3, the dimethyl amino series being basically similar. A good
17 agreement is found between our structural results and those obtained at a higher level of
18 theory by Champagne and coworkers on **1**, **2** and **3** [4d]. Relevant computed data are given in
19 Table 5. Discarding the substituents on N(3) and (if any) N(2), compounds **1**, **2**, **5**, **6**, **9** and **11**
20 are almost perfectly planar, whereas compounds **3**, **4**, **7**, **8**, **10** and **12**, which bear two six-
21 membered neighboring rings in their central backbone, exhibit an angle of 24-31° between the
22 two planes of these C₆ rings, due to steric hindrance. Nevertheless, this moderate out-of-plane
23 distortion still allows conjugation, as exemplified by the rather short inter-ring distance (1.46-
24 1.47 Å). In the diphenylamino series (Figure 3), the amino phenyl groups make an angle of
25 42-50° between them. As expected, all the computed molecules are strongly conjugated, as
26 exemplified by planar (sp²) bonding mode of the N(3) amino atom and the short N(3)-
27 C(spacer) distance (1.35-1.40 Å). As expected, the corresponding values reported in Table 5
28 indicate stronger conjugative for dimethylamino rather than diphenylamino groups and for D
29 = NR₂ rather than D = (C₆H₄)-NR₂. The averaged bond length alternation (BLA) index of the
30 C(1)-C(7) string is also a good descriptor of conjugation for such compounds (BLA = [d_{C(1)-}
31 d_{C(5)} + d_{C(6)-C(7)} - 2 x d_{C(5)-C(6)}]/2) [7]. The BLA values reported in Table 5 are all lower than
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4 0.12 Å, *i.e.* indicating significant conjugative effect. The lowest BLA values (thus the
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6 strongest conjugation) correspond to the methylated cations. The presence of a W(CO)₅
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8 moiety on N(2) also increase conjugation, but to a lesser extent. As already found by
9
10 Champagne and coworkers [7], the presence of two, rather than one, C₆ rings on the spacer
11
12 does not increase the conjugation. This is mainly due to the fact that the two neighboring rings
13
14 cannot be coplanar.
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17 The donor and acceptor fragment NPA charges are given in Table 5, together with the
18
19 computed dipole moments of the neutral species (solvent effects considered). One can see that
20
21 complexing the pyrimidine by W(CO)₅ considerably increases the polarity of the molecule.
22
23 Discarding the counter-anion effect, the methyl-substituted cationic species exhibit also
24
25 significant acceptor-donor charge separation, especially compounds **10** and **12**.
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29 <Figure 4>
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33 The MO diagrams of compounds **1-12** are quite similar. Those of **1** (D = NMe₂) and **3**
34
35 (D = C₆H₄NMe₂) are shown in Figure 4. They exhibit a rather high-lying π-type HOMO
36
37 which is mainly localized on the donor side of the molecule, whereas their π* LUMO has a
38
39 dominant acceptor (pyrimidine) character. Adding a supplementary C₆H₄ ring in the donor
40
41 fragment (compound **3**) induces the existence of a supplementary level below the HOMO,
42
43 which is of dominant spacer character. The presence of an acceptor W(CO)₅ or CH₃⁺
44
45 substituent on the pyrimidine does not perturb that much this general frontier MO picture,
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47 except that the polarities of the above-mentioned orbitals increase. In all the cases of the
48
49 organometallic derivatives, the three occupied 4d-type orbitals associated with the W(0)
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51 center lie below the HOMO and are not involved in the UV-vis optical transitions, as shown
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53 by the TD-DFT calculations of which the computed absorption transitions of lower energies
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55 and significant oscillation factors are reported in Table 1. A rather good agreement with
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4 experiment is found for compounds **1-2** and **5-9** for which the computed wavelength
5
6 correspond to a HOMO to LUMO transition, thus to a donor to acceptor charge transfer. In
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8 the case of compounds **3, 4, 10** and **12**, which all have a C₆H₄NR donor group, two transitions
9
10 of large oscillator strength are computed, which correspond to the HOMO to LUMO and
11
12 HOMO-1 to LUMO transitions, respectively. Their organometallic relatives **7** and **8** exhibit a
13
14 similar transition, but mainly involving the HOMO-4, due to intercalation of the three
15
16 occupied 4d-type orbitals. It is noteworthy that the wavelength corresponding to these two
17
18 OS-weighted averaged transitions (392, 388, 471, 430 and 477 nm for **3, 4 7, 8** and **10**,
19
20 respectively) are close to experimental λ_{max} values reported in Table 1. The S₁ to S₀ emission
21
22 wavelengths have also been computed (Table 1). Again, a rather good agreement is found
23
24 with the experimental PL λ_{max} values. These results confirm the nature of the S₁ which is a
25
26 donor-to-acceptor excited state.
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31 The optical hyperpolarizabilities have been also computed for compounds **1-12** (see
32
33 computational details). The β_{static} and β_{dynamic} (at 1907 nm) values are reported in Table 5.
34
35 Although such computed results have to be taken only at a qualitative level, one can notice
36
37 that they are rather consistent with the experimental EFISH data of Table 4. The methylated
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39 derivative, and to a lesser extent their organometallic relatives are particularly suited for
40
41 having interesting second-order NLO properties.
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45 <Table 5>
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50 **3. Conclusion**

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52 In conclusion, we have successfully synthesized and characterized push-pull 4-(arylviny)-
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54 1-methylpyrimidinium derivatives and a series of tungsten pentacarbonyl complexes of 4-
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56 (arylviny)pyrimidine. The optical properties including the second order nonlinear optical
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58 properties of the dyes were studied and compared to the corresponding 4-
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4 (arylvinyl)pyrimidines. Large and positive $\mu\beta$ values were measured for all the compounds by
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6 EFISH method. A strong increase of the $\mu\beta$ values were observed upon methylation and to
7
8 lesser extend upon complexation by $W(CO)_5$. According to experimental data supported by
9
10 DFT theoretical calculations, the photophysical properties of these new NLO organic
11
12 materials have been methodically untangled. Further investigation to combine an extension of
13
14 the conjugation with the enhancement of the attracting strength of the pyrimidine ring are
15
16 currently underway.
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19 20 **4. Experimental section**

21 22 *4.1. General methods*

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24 In air and moisture-sensitive reactions, all glassware was flame-dried and cooled under
25
26 nitrogen. Compounds **1-4** were synthesized according to reported procedure [6]. NMR spectra
27
28 were acquired at room temperature on a Bruker AC-300 or Bruker DRX500 spectrometers.
29
30 Chemical shifts are given in parts per million relative to $CDCl_3$ (1H : 7.26 ppm, ^{13}C : 77.0 ppm)
31
32 or $dmsO-d_6$ (1H : 2.50 ppm, ^{13}C : 39.4 ppm). Acidic impurities in $CDCl_3$ were removed by
33
34 treatment with anhydrous K_2CO_3 . High resolution mass analyses were performed at the
35
36 “Centre Régional de Mesures Physiques de l’Ouest” (CRMPO, University of Rennes1) using
37
38 a Bruker MicroTOF-Q II apparatus. IR spectra were recorded on a Perkin–Elmer
39
40 spectrum1000 FTIR using KBr plates. UV/vis spectra were recorded with a UVIKON xm
41
42 SECOMAM spectrometer using standard 1 cm quartz cells. Fluorescence spectra were
43
44 recorded using Spex FluoroMax-3 Jobin-Yvon Horiba apparatus. Measurements were
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46 performed at room temperature with solutions of $OD < 0.1$ to avoid re-absorption of the
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48 emitted light, and data were corrected with a blank and from the variations of the detector
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50 with the emitted wavelength.
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4 *4.2. General procedure for the complexation of pyrimidinyl derivatives by W(CO)₅(THF)*

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6 *reagent: synthesis of the pentacarbonyl complexes 5-8.*

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8 W(CO)₆ (352 mg, 1.0 mmol) was dissolved in degassed THF (75 mL). The solution was
9 irradiated with a medium pressure mercury vapor lamp under a slight N₂ positive pressure for
10 2.5 h. The yellow solution of W(CO)₅THF was transferred via cannula to a schlenk tube
11 charged with 0.6 mmol of pyrimidine derivative. The solution was stirred 2 h at rt under N₂
12 atmosphere. Concentration of the solvent under vacuum afforded a red solid which was
13 crystallized from CH₂Cl₂/*n*-heptane
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21 *4.3. Pentacarbonyl complex 5*

22 Red solid; 260 mg (79%); mp: 158-159°C; ¹H NMR (300MHz, CDCl₃): δ 3.08 (s, 6H), 6.73
23 (d, 2H, *J* = 8.7 Hz), 6.81 (d, 1H, *J* = 15.6 Hz), 7.11 (d, 1H, *J* = 6.0 Hz), 7.54 (d, 2H, *J* = 8 Hz),
24 7.95 (d, 1H, *J* = 15.6 Hz), 8.71 (d, 1H, *J* = 6.0 Hz), 9.22 (s, 1H); ¹³C NMR and JMOD
25 (75MHz, CDCl₃) δ 202.0 (CO), 198.4 (CO), 163.4 (C), 162.8 (CH), 160.8 (CH), 152.0 (C),
26 141.7 (CH), 130.1 (CH), 122.7 (C), 118.2 (CH), 118.1 (CH), 112.0 (CH), 40.1 (CH₃); IR
27 (KBr): ν = 2071 (CO), 1968 (CO), 1911 (CO) cm⁻¹; MS (ESI+) *m/z*: 549 [M]⁺. Anal. Calcd
28 for C₁₉H₁₅N₃O₅W: C, 41.55; H, 2.75; N, 7.65. Found C, 41.77; H, 3.89; N, 7.40.
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41 *4.4. Pentacarbonyl complex 6*

42 Red solid; 278 mg (69%); mp: 160-161°C; ¹H NMR (300MHz, CDCl₃): δ 6.89 (d, 1H, *J* =
43 15.9 Hz), 7.05 (d, 2H, *J* = 8.7 Hz), 7.18-7.11 (m, 7H), 7.36-7.31 (m, 4H), 7.48 (d, 2H, *J* = 8.7
44 Hz), 7.95 (d, 1H, *J* = 15.9 Hz), 8.79 (d, 1H, *J* = 6.0 Hz), 9.28 (s, 1H); ¹³C NMR and JMOD
45 (75 MHz, CDCl₃) δ 201.9 (CO), 198.4 (CO), 162.93 (C), 162.88 (CH), 161.2 (CH), 150.2 (C),
46 146.7 (C), 140.7 (CH), 129.6 (CH), 129.5 (CH), 127.7 (C), 125.6 (CH), 124.3 (CH), 121.4
47 (CH), 120.7 (CH), 118.7 (CH); IR (KBr): ν = 2071 (CO), 1967 (CO), 1900 (CO) cm⁻¹; MS
48 (ESI-) *m/z*: 708 [M+Cl]⁻, 1381 [2M+Cl]⁻. Anal. Calcd for C₂₄H₁₉N₃O₅W: C, 51.73; H, 2.84;
49 N, 6.24. Found C, 51.87; H, 3.09; N, 5.84.
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4 *4.5. Pentacarbonyl complex 7*
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6 Red solid; 273 mg (73%); mp 212°C (dec.); ¹H NMR (300MHz, CDCl₃): δ 3.04 (s, 6H), 6.83
7 (d, 2H, *J* = 8.7 Hz), 7.05 (d, 1H, *J* = 15.6 Hz), 7.22 (d, 1H, *J* = 6.0 Hz), 7.59 (d, 2H, *J* = 8 Hz),
8 7.66 (s, 4H), 8.05 (d, 1H, *J* = 15.6 Hz), 8.84 (d, 1H, *J* = 6.0 Hz), 9.33 (s, 1H); ¹³C NMR and
9 JMOD (75 MHz, CDCl₃) δ 201.9 (CO), 198.4 (CO), 162.9 (CH), 162.8 (C), 161.5 (CH),
10 150.4 (C), 143.4 (C), 140.9 (CH), 132.3 (C), 128.8 (CH), 127.7 (CH), 127.5 (C), 126.5 (CH),
11 122.5 (CH), 119.0 (CH), 112.7 (CH), 40.4 (CH₃); IR (KBr): ν = 2071 (CO), 1967 (CO), 1902
12 (CO) cm⁻¹; MS (ESI+) *m/z*: 626 [M+H]⁺. Anal. Calcd for C₂₅H₁₉N₃O₅W: C, 48.02; H, 3.06;
13 N, 6.72. Found C, 47.87; H, 3.18; N, 6.47.
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24 *4.6. Pentacarbonyl complex 8*
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26 Red solid; 355 mg (79%); mp 124°C (dec.); ¹H NMR (300MHz, CDCl₃): δ 7.11-7.05 (m,
27 3H), 7.18-7.15 (m, 6H), 7.24 (dd, 1H, *J*₁ = 6.0 Hz, *J*₂ = 0.9 Hz), 7.33-7.29 (m, 4H), 7.54 (d,
28 2H, *J* = 8.7 Hz), 7.66 (d, 2H, *J* = 8.7 Hz), 7.71 (d, 2H, *J* = 8.7 Hz), 8.06 (d, 1H, *J* = 15.9 Hz),
29 8.87 (dd, 1H, *J*₁ = 6.0 Hz, *J*₂ = 0.9 Hz), 9.35 (s, 1H); ¹³C NMR and JMOD (75 MHz, CDCl₃)
30 δ 201.8 (CO), 198.4 (CO), 163.0 (CH), 162.7 (C), 161.6 (CH), 148.0 (C), 147.5 (C), 142.8
31 (C), 140.6 (CH), 133.3 (C), 133.2 (C), 129.4 (CH), 128.8 (CH), 127.6 (CH), 127.0 (CH),
32 124.6 (CH), 123.4 (CH), 123.3 (CH), 123.0 (CH), 119.0 (CH); IR (KBr): ν = 2071 (CO), 1977
33 (CO), 1916 (CO) cm⁻¹; MS (ESI+) *m/z*: 693 [M-2CO]⁺, 749 [M]⁺. Anal. Calcd for
34 C₃₅H₂₃N₃O₅W: C, 56.09; H, 3.09; N, 5.61. Found C, 56.27; H, 3.24; N, 5.45..
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48 *4.7. General procedure for the methylation of pyrimidinyl derivatives.*
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50 A mixture of pyrimidine derivative (1.0 mmol) and methyl iodide (2 mL) was stirred for 3h.
51 The methyl iodide was evaporated under vacuum. The crude product was used without further
52 purification.
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57 *4.8.(E)4-[2-(4-Diphenylamino-phenyl)-vinyl]-1-methyl-pyrimidin-1-ium iodide (9)*
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4 Green solid; 304 mg (62%); ^1H NMR (500MHz, dms o-d_6): δ 4.10 (s, 3H), 6.89 (d, 2H, J =
5 9.0 Hz), 7.21-7.14 (m, 6H), 7.33 (d, 1H, J = 15.5 Hz), 7.41-7.38 (m, 4H), 7.71 (d, 2H, J = 9.0
6 Hz), 8.04 (d, 1H, J = 6.5 Hz), 8.22 (d, 1H, J = 15.5 Hz), 8.95 (d, 1H, J = 6.5 Hz), 9.40 (s, 1H);
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11 ^{13}C NMR and JMOD (125 MHz, dms o-d_6) δ 167.3 (C), 150.7 (CH), 150.6 (C), 145.8 (C),
12 145.2 (CH), 131.0 (CH), 129.9 (CH), 126.7 (C), 125.9 (CH), 125.1 (CH), 120.3 (CH), 119.6
13 (CH), 118.4 (CH); HRMS (ESI/ASAP) m/z calculated for $\text{C}_{25}\text{H}_{22}\text{N}_3$ $[\text{M}]^+$ 364.1814, found
14 364.1813.
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20 4.9.(E)4-[2-(4'-Diphenylamino-biphenyl-4-yl)-vinyl]-1-methyl-pyrimidin-1-ium iodide
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22 (10)
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25 Green solid; 527 mg (93%); mp: 175-176°C ^1H NMR (500MHz, dms o-d_6): δ 4.14 (s, 3H),
26 7.02 (d, 2H, J = 9.0 Hz), 7.10-7.06 (m, 6H), 7.35-7.32 (m, 4H), 7.61 (d, 1H, J = 15.5 Hz),
27 7.69 (d, 2H, J = 9.0 Hz), 7.79 (d, 2H, J = 9.0 Hz), 7.91 (d, 2H, J = 9.0 Hz), 8.15 (d, 1H, J =
28 6.5 Hz), 8.32 (d, 1H, J = 15.5 Hz), 9.07 (d, 1H, J = 6.5 Hz), 9.50 (s, 1H); ^{13}C NMR and
29 JMOD (125 MHz, dms o-d_6) δ 167.2 (C), 151.6 (CH), 147.6 (C), 146.8 (C), 144.6 (CH), 142.3
30 (C), 132.9 (C), 132.2 (C), 129.8 (CH), 129.7 (CH), 127.8 (CH), 126.6 (CH), 124.5 (CH),
31 123.6 (CH), 123.2 (CH), 122.6 (CH), 119.3 (CH); HRMS (ESI/ASAP) m/z calculated for
32 $\text{C}_{31}\text{H}_{26}\text{N}_3$ $[\text{M}]^+$ 440.2127, found 440.2125.
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43 5. Computational details

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4 ionization energies and electron affinities discussed above have been calculated considering
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6 the energies of the optimized neutral and ionic structures (solvent corrections performed). The
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8 UV visible transitions were calculated by means of TDDFT calculations²⁷ at the same level of
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10 theory. Only singlet-singlet transitions have been taken into account. Only the transitions with
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12 non-negligible oscillator strengths are discussed in the paper. Static and frequency-dependent
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14 electronic (hyper)polarizability tensor components β_{ijj} ($i, j = x, y, z$) were obtained through
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16 the Coupled-Perturbed Hartree-Fock procedure²⁸ using the more appropriate wB97XD
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18 functional²⁹ with the same basis set as above. Dynamic (hyper)polarizabilities are computed
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20 assuming a laser wavelength of 1907 nm ($\hbar\omega = 0.023896$ a.u.) for the SHG [$\beta(-2\omega; \omega, \omega)$]
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22 NLO processes.
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31 **Acknowledgement.**

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33 JYS thanks the Institut Universitaire de France for support.
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38 **Supplementary informations**

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40 Supplementary data related to this article can be found at <http://dx.doi.org>
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4 **Scheme 1: Synthesis of compounds 5-8**

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6 **Scheme 2: Synthesis of compounds 9-12**

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11 **Table 1. UV/Vis and photoluminescence (PL) data**

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13 **Table 2. Absorption maxima of 9 in various solvents**

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15 **Table 3. Absorption maxima of CH₂Cl₂ solution of 9 at various concentrations.**

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17 **Table 4. $\mu\beta$ values for compounds 1-10**

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19 **Table 5. Selected computed data (solvent corrections considered).**

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34 **Figure 1: Normalized UV/vis of compounds 2, 6 and 9 in CH₂Cl₂.**

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36 **Figure 2: Normalized UV/vis of compounds 9 in various solvents.**

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38 **Figure 3. Optimized molecular structures of the computed diphenylamino derivatives.**

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41 **Figure 4. MO diagrams on 1 and 3. The numbers correspond to the following fragment**
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43 **localisations (%): pyrimidine (nitrogen atoms)/ C(5)=C(6)/C₆ ring(s)/amine group(N).**

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Table1

Compd ^a	UV/vis λ_{max} , nm	Computed absorption transition (nm) and OS ^e	Computed emission transition (nm) ^e	PL		Stokes shift cm ⁻¹
	(ϵ , mM ⁻¹ ·cm ⁻¹)			λ_{max} , nm	Φ_F ^b	
1^c	393 (28.6)	411 (1.20)	473	488	0.15	4953
2^c	400 (32.0)	438 (1.10)	520	526	0.45	5989
3^c	386 (32.4)	451 (1.09) 322 (0.66)	542	570	0.66	8362
4^c	384 (35.4)	452 (0.99) 339 (0.97)	548	564	0.52	8280
5	462 (31.3)	459 (1.51)		_d	_d	_d
6	462 (33.4)	486 (1.44)		_d	_d	_d
7	443 (27.2)	507 (1.31) 335 (0.23)		_d	_d	_d
8	435 (28.6)	506 (1.14) 352 (0.77)		_d	_d	_d
9	564 (40.3)	534 (1.35)		_d	_d	_d
10	520 (34.6)	633 (0.83) 402 (1.09)		_d	_d	_d
11^f		482 (1.47)				
12^f		617 (1.12) 378 (0.82)				

^a All spectra were recorded in CH₂Cl₂ solutions at room temperature at $c = 1.0 \times 10^{-5}$ M to 3.0×10^{-5} M for absorption and $c = 1.0 \times 10^{-6}$ M to 3.0×10^{-6} M for emission. ^b Fluorescence quantum yield ($\pm 10\%$) determined relative to quinine sulfate in 1 M H₂SO₄ ($\Phi_F = 0.54$). ^c results from ref. [6]. ^d: no fluorescence detected. ^e From TD-DFT calculations. OS = oscillation strength factor. ^f hypothetical compound.

Table2

	<i>n</i> -heptane	Toluene	THF	CHCl ₃	CH ₂ Cl ₂	MeCN	DMSO	MeOH
UV/vis λ_{max} , nm	503	521	507	545	550	502	492	506

Table3

Concentration (M)	$7.34 \cdot 10^{-6}$	$1.47 \cdot 10^{-5}$	$2.20 \cdot 10^{-5}$	$2.54 \cdot 10^{-5}$	$7.35 \cdot 10^{-5}$
UV/vis λ_{max} , nm	564	556	554	552	546
($\epsilon, \text{mM}^{-1} \cdot \text{cm}^{-1}$)	(40.3)	(39.3)	(40.7)	(40.4)	(37.5)

Table4

	1	2	3	4	5	6	7	8	9	10
$\mu\beta$ [10^{-48} esu]^a	330	190	470	200	770	700	490	460	2350	1080

^a: $\mu\beta$ (2ω) at 1907 nm in CHCl_3 . Molecular concentrations used for the measurements were in the range 10^{-3} to 10^{-2} M. $\mu\beta \pm 10\%$.

Table5

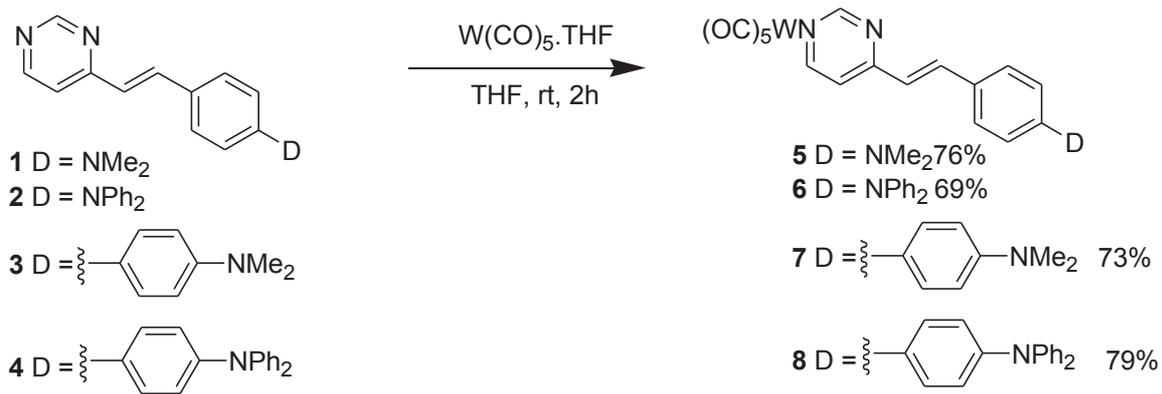
	1	2	3	4	5	6	7	8	9	10	11	12
HOMO/LUMO gap (eV)	3.52	3.39	3.21	3.21	3.20	3.09	2.89	2.89	2.72	2.31	2.91	2.34
Distances (Å):												
C(1)-C(2)	1.400	1.398	1.397	1.397	1.403	1.400	1.399	1.398	1.413	1.409	1.416	1.411
C(2)-N(1)	1.347	1.345	1.344	1.344	1.350	1.348	1.347	1.346	1.356	1.352	1.360	1.354
N(1)-C(4)	1.321	1.321	1.321	1.321	1.310	1.310	1.311	1.311	1.297	1.299	1.296	1.298
C(4)-N(2)	1.331	1.331	1.331	1.331	1.342	1.342	1.342	1.342	1.347	1.346	1.347	1.346
N(2)-C(3)	1.336	1.335	1.334	1.334	1.346	1.345	1.344	1.343	1.353	1.351	1.355	1.352
C(3)-C(1)	1.378	1.379	1.380	1.380	1.370	1.372	1.373	1.373	1.359	1.361	1.357	1.360
C(5)-C(6)	1.348	1.345	1.344	1.343	1.353	1.349	1.347	1.345	1.360	1.353	1.365	1.356
BLA ^a	0.097	0.104	0.108	0.110	0.084	0.094	0.099	0.103	0.067	0.082	0.055	0.076
C(ring)-C(ring): [range] average	[1.375-1.416] 1.398	[1.377-1.403] 1.394	[1.381-1.409] 1.395	[1.379-1.402] 1.393	[1.373-1.417] 1.398	[1.376-1.405] 1.394	[1.378-1.410] 1.395	[1.379-1.403] 1.394	[1.371-1.410] 1.396	[1.376-1.405] 1.394	[1.368-1.417] 1.399	[1.37-1.412] 1.396
C(10/16)-N(3)	1.357	1.396	1.367	1.402	1.354	1.391	1.365	1.401	1.379	1.396	1.346	1.357
N(3)-C(R)	1.445	1.414	1.444	1.411	1.446	1.416	1.444	1.412	1.420	1.413	1.448	1.444
W-N(2)/Me-N(2)					2.289	2.291	2.293	2.291	1.460	1.461	1.461	1.460
NPA fragment charges:												
A ^b	-0.14	-0.12	-0.11	-0.10	-0.41	-0.16	-0.15	-0.14	0.70	0.20	0.41	0.17
D ^b	0.07	-0.08	0.05	0.03	0.08	-0.06	0.07	0.04	0.00	0.43	0.13	0.52
NR ₂	0.07	-0.08	0.03	-0.11	0.08	-0.06	0.04	-0.11	0.00	0.59	0.13	0.68
Dipole moment (Debye)	9.8	6.2	9.0	5.6	19.1	15.3	17.9	14.0				
β _{static} (10 ⁻³⁰ esu)	103	96	112	90	151	140	157	119	307	285	264	386
β _{dynamic} (10 ⁻³⁰ esu) ^c	133	124	144	115	204	189	208	155	458	403	395	574

^a Bond length alternation index : BLA = $[d_{C(1)-C(5)} + d_{C(6)-C(7)} - 2 \times d_{C(5)-C(6)}]/2$ (see Figure 3).

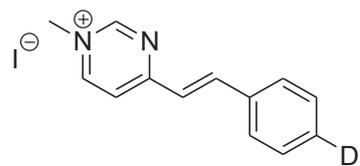
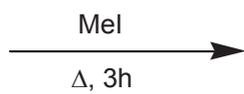
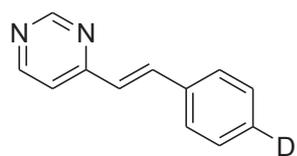
^b A = acceptor (pyrimidine or substituted pyrimidine); D = donor, as defined in Schemes 1 and 2.

^c Assuming a 1907 nm laser wavelength.

Scheme 1



Scheme2



9 D = NPh₂ 62%

10 D = -NPh₂ 93%

11 D = NMe₂ *non isolated*

12 D = -NMe₂ *non isolated*

Figure1

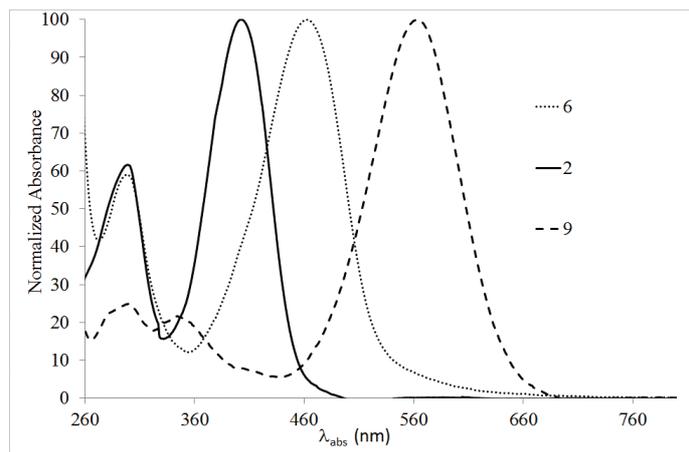


Figure2

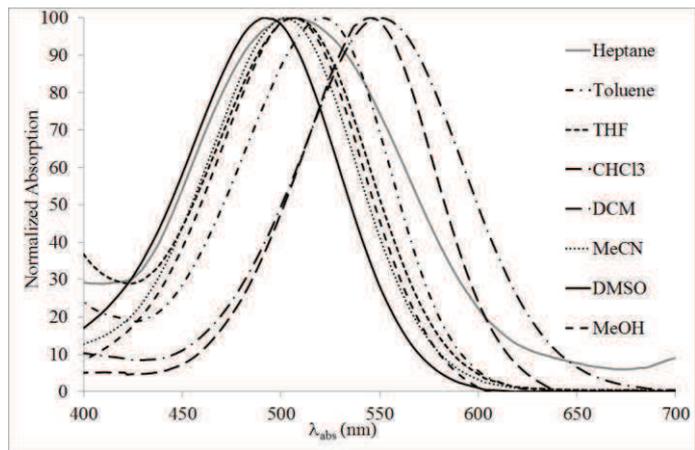
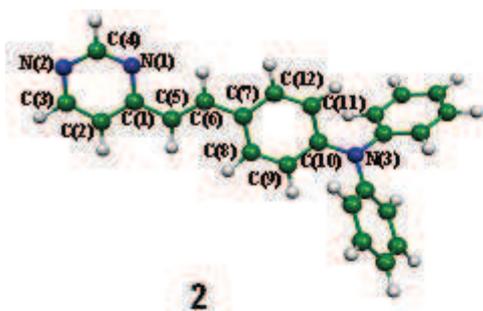
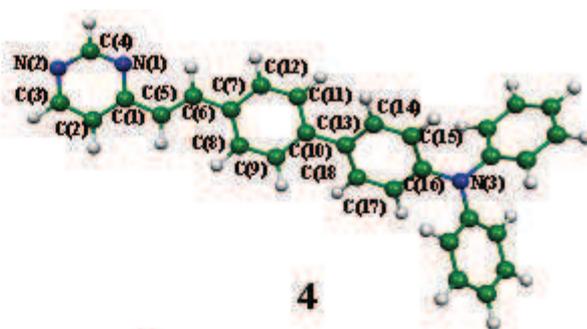


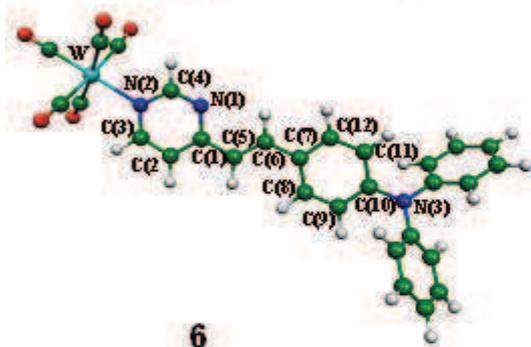
Figure3



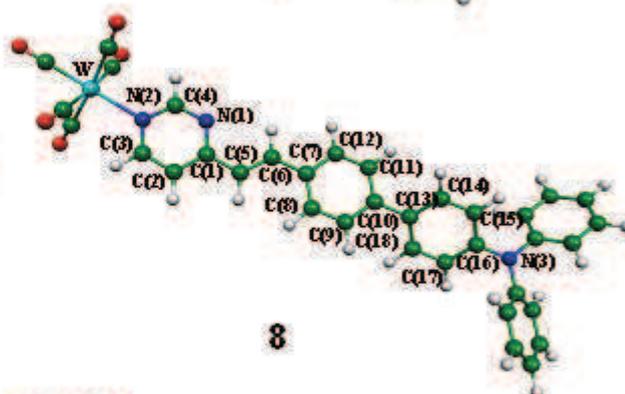
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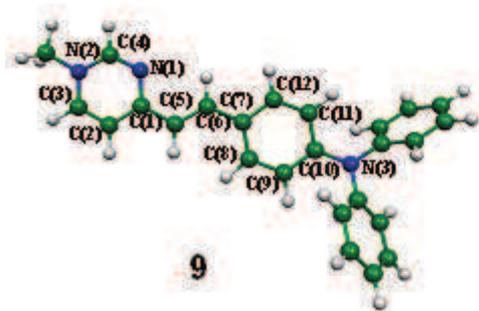
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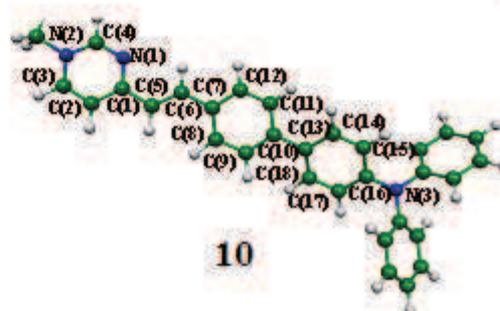
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Figure4

