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Abstract A series of pyridinium-betaine like molecules has been reported; one family of molecules is built with a benzimidazole core and a second one with a pyrimidine moiety. The title compounds were prepared by mixing 2-chlorobenzimidazole or 2-bromopyrimidine with the corresponding pyridines (pyridine, 4-*tert*-butylpyridine, 4-hydroxypyridine, potassium 4-trifluoroboratepyridine, 4-dimethylaminopyridine) in acetonitrile or DMSO at high temperatures. The novel compounds were characterized by spectroscopic methods. The UV-Vis. and fluorescence features are reported as well. Preliminary photoluminescence results showed broadband emissions as common feature ascribed to the compounds containing benzimidazole ring. Some of the spectra nearly span over the whole visible spectral range, which pave the way to real opportunities to design single-component panchromatic emitters.

Keywords Pyridinium ● Betaines ● Fluorescence ● Absorption

✉ Dr. Jamal Moussa
jamal.moussa@sorbonne-universite.fr

Institut Parisien de Chimie Moléculaire UMR 8232, Sorbonne Université, 4 place Jussieu, 75252 Paris cedex 05, France.

Introduction

Pyridinium-betaine dyes are a fascinating class of compounds, especially due to their exceptional photophysical properties related to the presence of low-lying intramolecular charge-transfer (CT) excited states.[1-4] In particular, these compounds usually exhibit large negative solvatochromism because of a dramatic reduction of the dipole moment between the ground and the excited states; this has led to the development of general methods for solvents polarity measurements.[5] An important other feature is a large first-order hyperpolarizability and thus large non-linear optical response resulting from the dipole moment change which makes these molecules very attractive compounds for NLO applications.[6-7]

On the other hand since the pioneering work by the groups of Breslow,[8] Wanzlick[9] and Öfele[10] and the isolation of the first stable metal free carbenes by Bertrand et al.[11] and Arduengo et al.[12] the chemistry of N-heterocyclic carbenes has developed remarkably because of their peculiar stereoelectronic properties especially their exceptional σ-donor capacity in catalytically active metal complexes.[13] Meanwhile, several classes of N-heterocyclic carbenes have been discovered, among others pyridylidenes remain relatively unexplored as a result of tedious and non-general synthetic methods of such species.[14-19]

Although the chemistry of N-heterocyclic carbenes (NHCs) and the chemistry of heterocyclic mesomeric betaines (MB) have a common area, there are very few compounds exhibiting both functionalities. Betaines are molecules that can be represented by only one dipolar canonical formula in which the positive and negative charges are delocalized within a common π-electron system. There are several relationships that link the salts of *N*-heterocyclic carbenes and mesomeric betaines, for instance interesting results have been recently reported by Schmidtt et al. with pyridinium-2-carboxylates that evolve to *N*-heterocyclic carbenes.[20]

We describe here a simple synthesis of pyridinium-betaine compounds in the view to utilize them later as bidentate chelating *N^C* heteraryl-pyridylidene ligands. The target compounds are shown in Figure 1; We believe that this type of molecules represents a real opportunity for the development of a new class of bidentate ligands exhibiting rare pyridylidene centres combined with other nitrogen or heteroatom donors to provide unprecedented transition metal complexes with multiple potential applications in luminescent materials or catalysis for example. The chemistry and the results of such compounds will be reported in the near future and in the adequate journals.

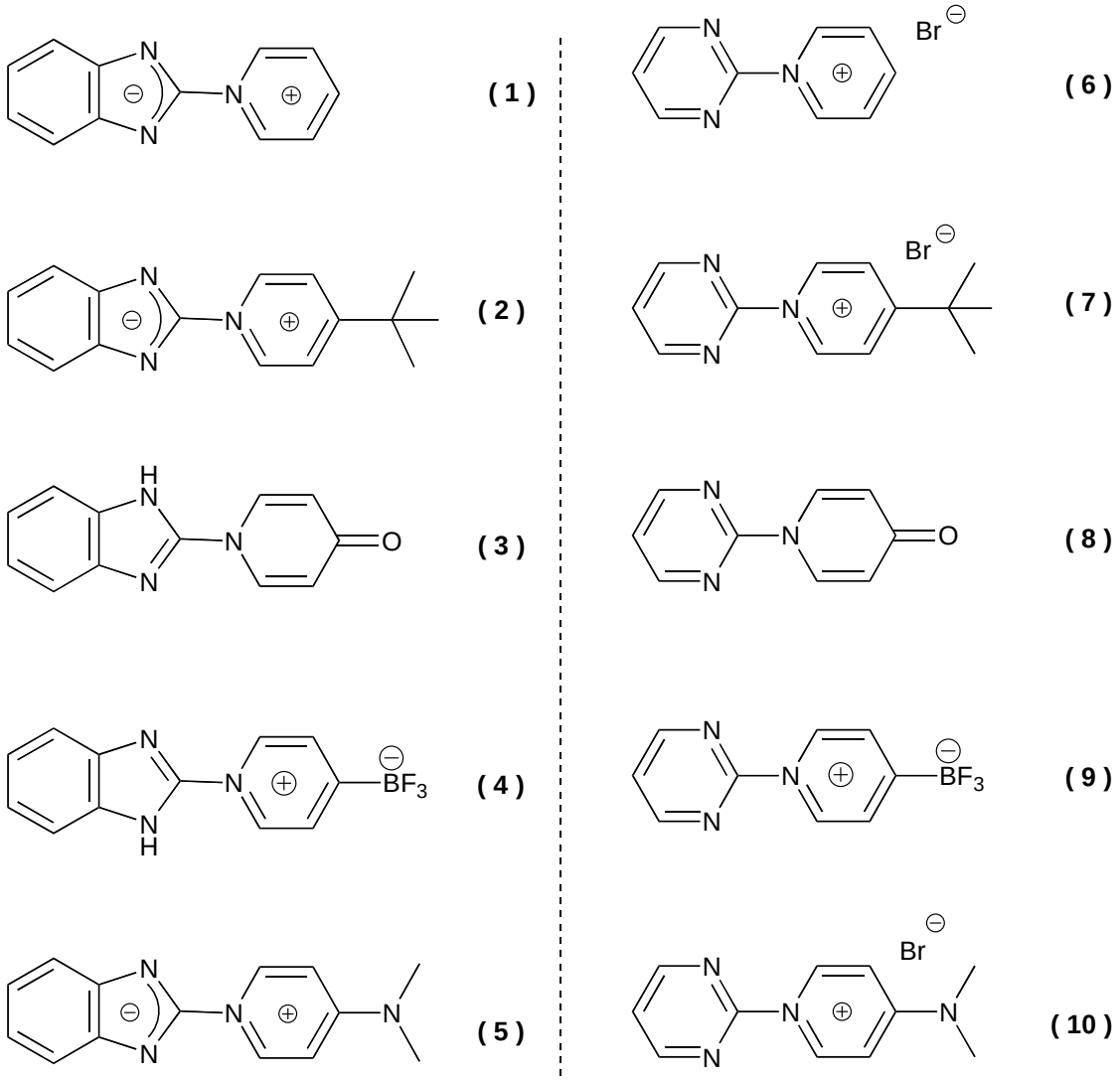


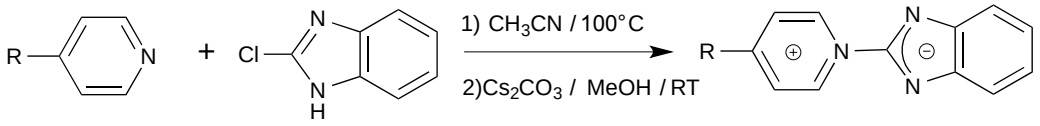
Figure 1: Novel pyridinium-benzimidazole and pyridinium-pyrimidine scaffolds.

Results and Discussion

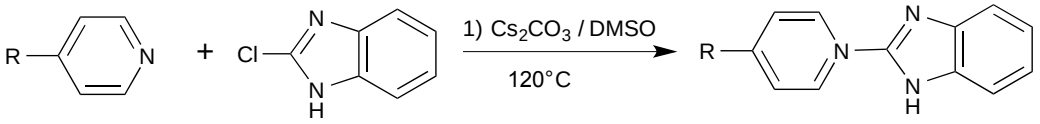
Synthesis and characterization

The synthetic routes leading to compounds **1-5** are depicted in scheme 1. Treatment of 2-chlorobenzimidazole with an excess of pyridine in acetonitrile under reflux and subsequent reaction work-up provided the

target molecule in good yield. The resulting compound is obtained upon substitution of the chloride atom by pyridine and consists of a benzimidazole moiety linked through the C2 carbon to the nitrogen of the pyridine providing a pyridinum chemical structure. The unreacted 2-chlorobenzimidazole crystalizes as white needles and is separated by filtration on a sintered glass funnel. Then treatment with cesium carbonate provided compound **1** reproductively in good yields. Identification of the compound was unambiguously achieved by spectroscopic methods. For instance, the ^{1}H-NMR spectrum of 2-pyridinumbenzimidazole (**1**) in CD_3CN shows a series of signals in the aromatic region due to the protons of the pyridinium and the benzimidazole moieties. A typical set of signals of an AA'BB' system attributable to the benzimidazole protons is observable at δ = 7.08 ppm and δ = 7.57 ppm, finally two triplets and one doublets are visible at δ = 8.06 ppm, δ = 8.48 ppm and δ = 9.99 ppm. This compound was described in the literature using a different synthesis method without NMR characterization.[21]



R = -H, t-Bu, NMe_2 R = -H (**1**), -t-Bu(**2**), -NMe_2 (**5**)



R = -OH, -BF_3- R = -O (**3**), -BF_3 (**4**)

Scheme 1: Synthesis of the pyridinium-betaine molecules with the benzimidazole core (**1-5**)

Under the reaction conditions for the preparation of compound **1**, using 4-tert-butylpyridine instead of pyridine gave compound **2**. The molecular weight of the target molecule was determined by mass spectroscopy (252.1505 $g.mol^{-1}$) and further characterization by ^{1}H- and ^{13}C-NMR spectroscopy confirmed the identity of the novel compound **2**. (see experimental part for details).

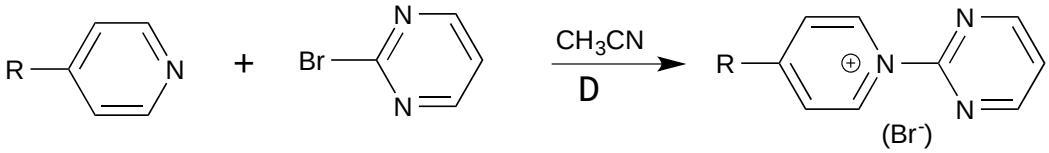
Using 4-hydroxypyridne instead of pyridine or 4-tert-buthylpyridine in these reaction conditions did not allow obtaining the target compound. However using DMSO as solvent and under high temperature conditions, in presence of sodium or caesium carbonate provided finally the desired molecule **3** in good yield. Molecule **3** is a pyridone core linked through the nitrogen to C2 carbon of the benzimidazole moiety. It was identified by

NMR and infrared spectroscopy techniques. The molecular weight of the target molecule was determined by mass spectroscopy (234.0638 $g.mol^{-1}$). (see experimental part for details). These reaction conditions using 4-trifluoroboratepyridine instead of 4-hydroxypyridine but in absence of carbonates provided the zwiterrion **4** in good yield. Identification of the compound was unambiguously achieved by ^{1}H- and ^{13}C-NMR and infrared spectroscopic methods. Evidence of the molecular weight of the molecule emanates from mass spectroscopy (262.0761 $g.mol^{-1}$). (Structural details are given in the experimental part)

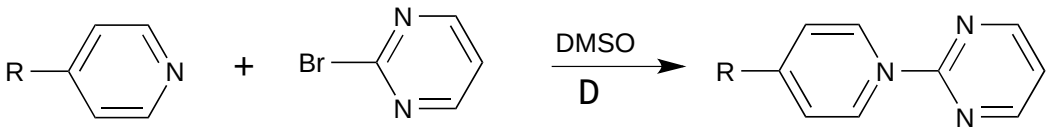
The last molecule of this series is prepared by reaction 2-chlorobenzimidazole with 4-dimethylaminopyridine using the experimental conditions to prepare compound **3**. The target compound **5** is obtained in good yield. The identity of the new compound was clearly ascertained by ^{1}H-NMR and infrared spectroscopic methods. Confirmation of the molecular weight of the isolated molecule is obtained from mass spectroscopy (239.1295 $g.mol^{-1}$).

We then decided to prepare analogous compounds of **1-5** exhibiting a pyrimidine core instead of the benzimidazole moiety. The desired novel compounds consist of a pyridinium moiety and a pyrimidine part that is expected to be more electron-withdrawing than a benzimidazole ring which might have a profound impact on the electronic properties of the target

final molecules and later on the metal complexes. The synthetic routes leading to compounds **6-10** are depicted in scheme 2.



R = -H, t-Bu, NMe_2 R = -H (**6**), -t-Bu(**7**), -NMe_2 (**10**)



R = -OH (+ Na_2CO_3), -BF_3^- R = =O (**8**), -BF_3^- (**9**)

Scheme 2: Synthetic routes to the novel compounds **6-10** based on the pyrimidine core

For instance when 2-bromopyrimidine is reacted with pyridine, the pyridine nitrogen displaces the bromine atom; an interesting cationic compound with a pyridinium core linked by the nitrogen atom to C2 carbon of a pyrimidine moiety is obtained in good yield. The ^{1}H-NMR spectrum of compound **6** exhibits a set of signals in the aromatic region. A doublet at δ = 9.12 ppm and a triplet at δ = 7.86 ppm are due to the pyrimidine moiety. Four other multiplets are observed due to the pyridinium core. Additional evidence of the molecular weight of the isolated molecule is given by mass spectroscopy (158.0712 g.mol^{-1}).

Starting with 4-tert-butylpyridine and 2-bromopyrimidine provided upon reaction workup compound **7** in good yield. Confirmation of the molecular weight of the isolated molecule is given by mass spectroscopy (214.1347 $g.mol^{-1}$). The identity of compound 7 was confirmed by ^{1}H-NMR, ^{13}C-NMR and infrared spectroscopic methods. (Structural details are given in the experimental part).

Similarly to the fist series with the benzimidazole moiety, reaction of 4-hydroxypyridine with 2-bromopyrimidine in acetonitrile did not offer the target compound. However in the presence of sodium carbonate in hot DMSO the target compound **7** was obtained in good yields. Additional evidence of the molecular weight of the isolated molecule is given by mass spectroscopy (196.0483 $g.mol^{-1}$). Compounds **9** and **10** were obtained under similar reaction conditions in good yields.

Having prepared these two families of compounds we decided to explore their absorption and emission properties since some of the molecules seemed to be highly luminescent under the UV lamp. Furthermore, as mentioned in the introduction we plan to use these compounds as ligands with transition metals so such a study is relevant to further comparison purposes.

UV-Vis. absorption and emission properties

The UV-Vis. spectra of all compounds were recorded in acetonitrile solutions at C ≈ 10^{-5} M. Spectra of compounds of the first family with the benzimidazole core are assembled in Figure 2. All spectra exhibit a high-energy absorption band with high molar absorptivity molar values typical of π–π* transitions. Distinct additional charge transfer type transitions at lower energy are visible for compounds **1**, **2** and **4**. The spectra of molecules **3** and **5** don't seem to clearly exhibit such charge transfer absorptions, maybe occurring at high energies thus overlapped with the π–π* transitions, tails on the high energy transitions are however visible. These assignments are in good agreement with the experimental and theoretical studies on the model compound **1**.[1a] In particular the authors have shown that the intramolecular charge transfer band in compound **1** was hypsochromically shifted from toluene to THF and acetonitrile. We have checked the charge transfer character of compounds **2** and **4** by recording the UV-vis. absorption spectra in dichloromethane. Both compounds **2** and **4** exhibited blue shifts from dichloromethane to acetonitrile of 18 nm and 14 nm respectively. (The spectra are provided in the supplementary section). Compounds **2-10** are not described in the literature but the close similarity of the data with those of compound **1** are in favour of the given assignments.

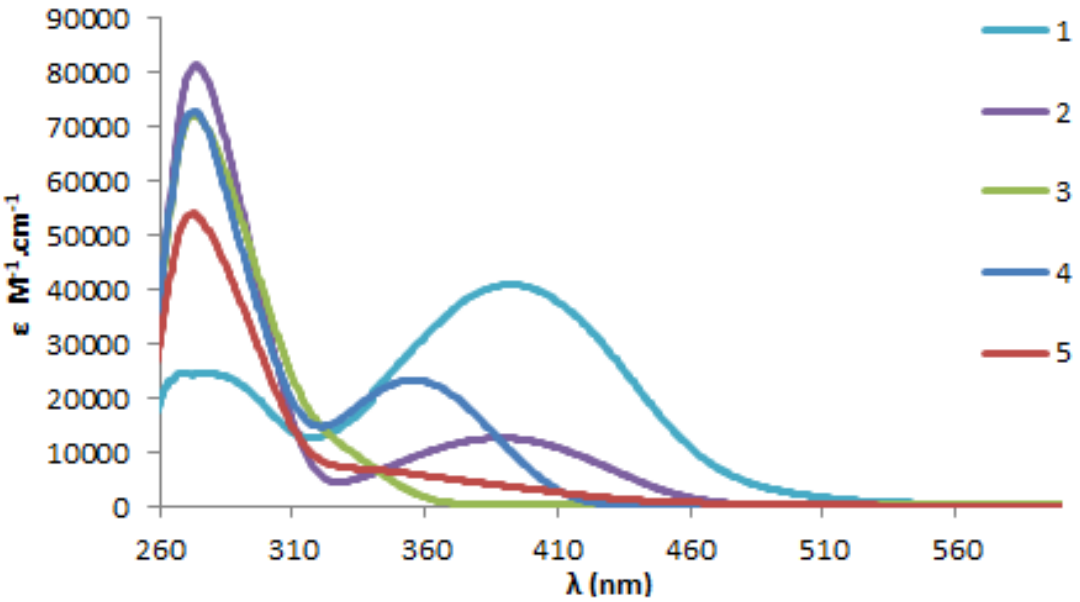


Figure 2: Absorption spectra of compounds **1-5** in acetonitrile

The UV-Vis. absorption spectra of compounds of the second family with the pyrimidine core (**6-10**) recorded in acetonitrile are shown in Figure 3 and the data are assembled in table 1. All spectra exhibit a high energy absorption transition around 270 nm with high molar absorptivity molar values typical of π–π* transitions with the exception of compound **10** which shows a significantly lower energy absorption at 320 nm. Within this family no charge transfer type transitions are detectable.

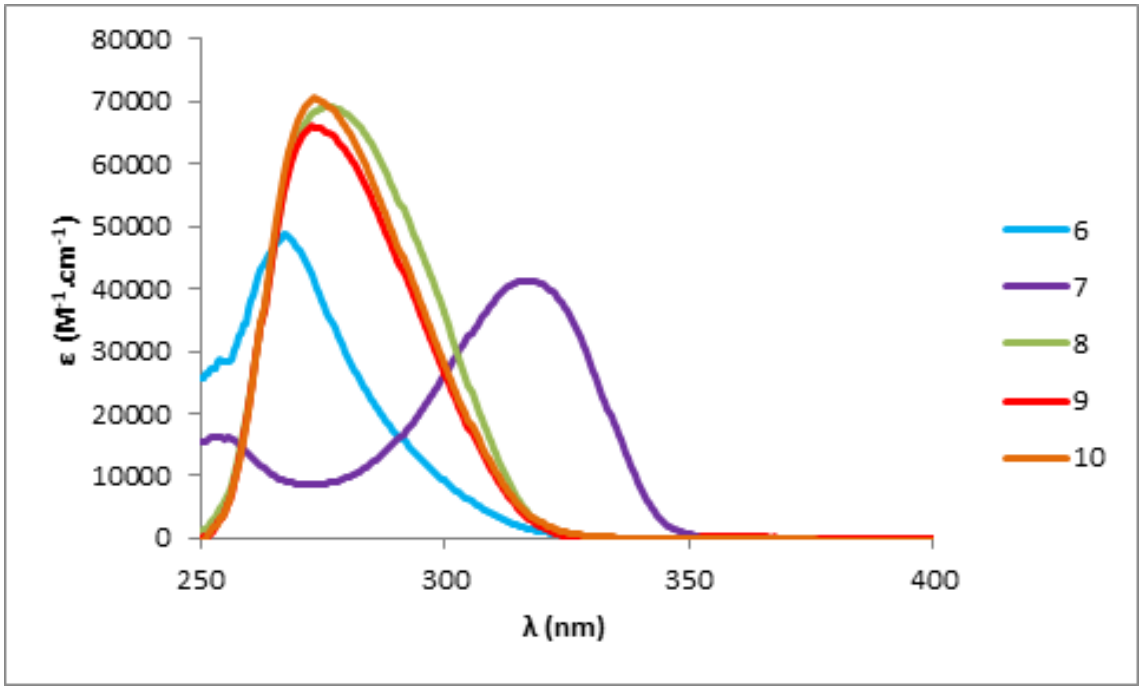


Figure 3: Absorption spectra of compounds **6-10** in acetonitrile

Table 1: UV-Vis. absorption data for compounds **1-10**

	λ_{abs} (nm)	ε ($mol^{-1}.L.cm^{-1}$)x10^4
1	269; 392	2.47; 4.09
2	273; 388	8.11; 1.27
3	273	7.21
4	273; 355	7.29; 2.34
5	272	5.39
6	267	4.87
7	317	4.13
8	277	6.91
9	273	6.59
10	273	7.04

Photoluminescence spectra of all compounds were recorded in air equilibrated dichloromethane solutions at C ≈ 10^{-5} M. Compounds **6-10** did not exhibit any emission upon excitations in the 300-340 nm. In stark contrast, solutions of compounds **1-5** exhibit relatively intense emissions upon excitation wavelengths in the range 350-400 nm. The spectra are

presented in figure 4. These data are only qualitative since our goal is to use these compounds to prepare pyridylidene metal complexes as mentioned in the introduction. The parent compound **1** was found to exhibit an emission at λ_{max}= 687 nm in acetonitrile with a blue shift in THF solution at λ_{max} = 675 nm and in toluene at λ_{max} = 669 nm, we found this emission to be at λ_{max} = 647 nm in dicholormethane solution at room temperature. Molecule **2** exhibits a similar emission band at λ_{max} = 627 nm in dichloromethane slightly blue shifted in comparison to the parent compound **1** due to presence of the tert-butyl- group. The pyridone derivative **3** has an interesting UV-blue emission while compounds **4** and **5** exhibit very unusual broad emission bands covering a wide region of the visible spectrum (400-680/690 nm). These unusual broad emission bands seem to be the result of a dual emission which make these molecules interesting candidates to design single-component panchromatic emitters.

To make sure that emissions do not arise from small highly emitting impurities, the excitation spectrum has been recorded in the excitation wavelengths range and fits well to the absorption spectrum in each case. White-light emission from a single component is quite rare in the literature; discovery of powerful molecules in this field would be of real application potential in lightening devices. Such behaviour in compounds **4** and **5** is very peculiar, as far as we are aware there is very few examples displaying

white light emission from a single-component described in the literature.[22-23] White light emission is usually obtained by combination of three different components (blue, green and red emitters), which makes the devices preparation and durability a complicated task.[24-26]

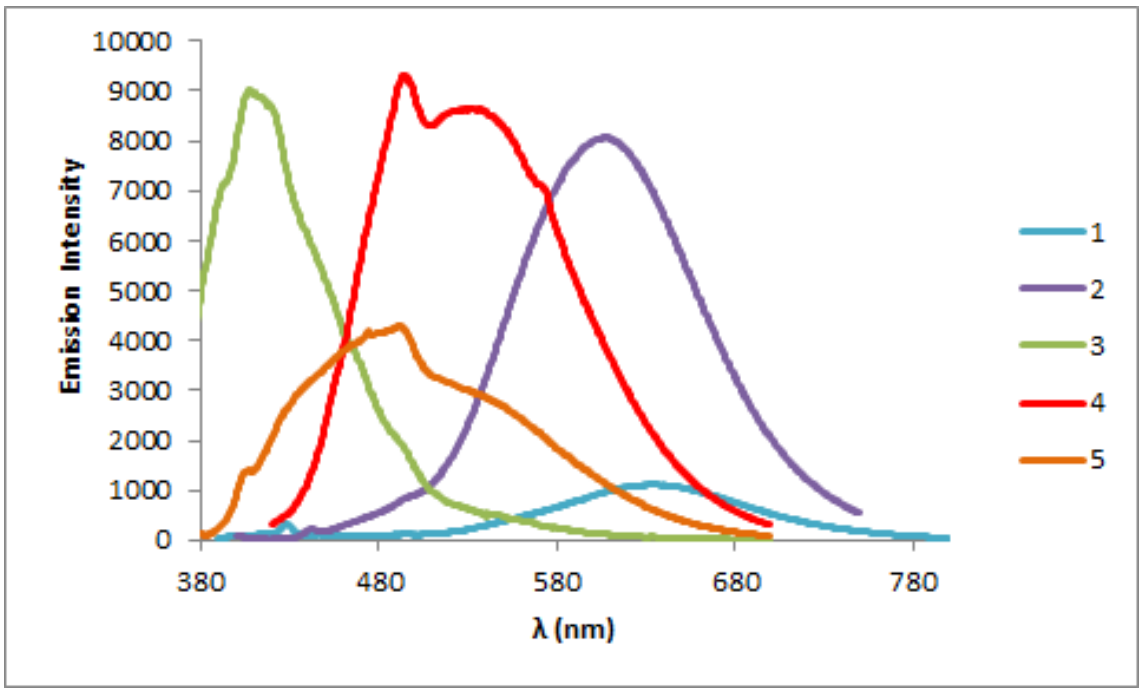


Figure 4: Photoluminescence spectra of compounds **1-5** in air equilibrated dichloromethane solutions.

We believe that detailed spectroscopic and theoretical investigations will be conducted in the future to unravel the properties of the excited states involved in these processes in order to understand the fundamental and crucial parameters to be controlled to lead to the discovery of very useful molecules with panchromatic emission properties.

Conclusion

In this work we set up general procedures to prepare two families of betaine like molecules based on benzimidazole or pyrimidine cores. Heating 2-chlorobenzimidazole or 2-bromopyrimidine with an excess of the corresponding pyridine (pyridine, 4-tert-butylpyridine, 4-hydroxypyridine, 4-trifluoroboratepyridine or 4-dimethylaminopyridine) in acetonitrile or dimethylsulfoxyde provides the target molecules in good to high yields. Identification of the compound was unambiguously achieved by spectroscopic methods and the molecular weight was confirmed by mass analyses. Furthermore, we have reported the UV-Vis. Absorption and emission properties of the new molecules **1-10**. Compounds of the pyrimidine core family are not emissive in air equilibrated dichloromethane solutions nor in the solid state but interesting photoluminescence results are obtained for the benzimidazole-based family (**1-5**). In particular some of the molecules clearly show a dual emission behaviour that make them emitting nearly over the whole visible spectral range providing a unique opportunity to design single-component white light emitting materials with great potential in the lighting technology. As an interesting perspective we believe that

these novel betainoid molecules may act as singular bidentate pyridylidene ligands for transition metal complexes. We will investigate their coordination properties in the near future and the results will be published in due course.

Experimental

Materials and Methods

All experimental manipulations were carried out under an argon atmosphere by using Schlenk tube techniques. Solvents were dried and distilled under argon by standard procedures. All reagents obtained from commercial sources were used as received. The ^{1}H and ^{13}C NMR spectra were recorded in CD_3CN using a Bruker Avance 300 NMR spectrometer at 300.13 MHz, and 75.47 MHz respectively. IR spectra were recorded on a Bruker Tensor 27 equipped with an ATR Harricks apparatus. UV-Vis. spectra were recorded on a *JASCO V-670* Spectrometer. Photoluminescence spectra were recorded using a *JASCO J-815 CD* Spectrometer. Mass spectrometric analyses of compounds **2**, **4**, **5**, **7**, **9**, and **10** were performed on a microTOF Bruker mass spectrometer (ESI-TOF). These compounds were performed in methanol by direct infusion with the ESI-source set at 180°C and a capillary voltage set at 4500 VMass spectrometric analyses of compounds **3**, **8** and **6** were performed on a LTQ Orbitrap high-resolution (Thermo). These compounds were dissolved in

methanol and analyzed by direct infusion with the positive mode Electrospray (ESI) source set at 275°C and a capillary voltage set at 20 V.

Compound 1, 2-pyridiniumbenzimidazolate: 2-chlorobenzimidazole (250 mg, 1,64 mmol) and anhydrous pyridine (1 mL) were placed in a Schlenk tube and acetonitrile (20 ml) was added. The mixture was refluxed under an atmosphere of argon at 100 °C for 48h. Then cooling the solution results in the precipitation of unreacted 2-chlorobenzimidazole as white crystalline needles that can be recovered on a sintered glass funnel. The filtrate is then evaporated to dryness and to the oily residue is added anhydrous diethyl ether (50 mL), a light-yellow solid formed and was recovered and dissolved in methanol in presence of Cs_2CO3 for 30 minutes. After evaporation to dryness, the solid residue was extracted with dichloromethane (3x15 mL), upon filtration through celite and evaporation of the volatiles; a yellow solid is obtained (288 mg, 1,47 mmol). Yield: 89 %.

IR (neat ATR Harricks, cm^{-1}): 3064, 2923, 1683, 1627, 1524, 1481, 1434, 1352, 1334, 1315, 1269, 1158, 1072, 1040, 952, 879, 856, 813, 742, 674, 615, 595, 551, 522, 503, 429, 376, 357, 309.

^{1}H NMR (300.13 MHz, CD_3CN): δ = 10.00 (d, 2H, ^{2}J = 6.9 Hz, H_α pyridinium), 8.42 (t, 1H, ^{2}J = 7 Hz, H_β pyridinium), 8.03 (dd, 2H, ^{2}J = 7 Hz, H_β pyridinium), 7.54 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_β benzimidazol), 7.04 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_α benzimidazol). $^{13}C\{^{-1}H\}$ NMR (75.47 MHz, DMSO-d_6) δ = 124.4, 128.1, 141.8, 145.3, 149.1,150.9.

Anal. Calcd. For $C_{12}H_9N_3$ (195.2 g.mol^{-1}): C, 73.83; H, 4.65; N, 21.52. Found: C, 74.31; H, 4.37; N, 21.11.

Compound 2, 2-4-*tert*-butylpyridiniumbenzimidazolate: 2-chlorobenzimidazole (540 mg, 3,54 mmol) and anhydrous 4-*tert*-butylpyridyl (1 mL) were placed in a Schlenk tube and acetonitrile (20 ml) was added. The mixture was refluxed overnight under an argon atmosphere at 100 °C. Then cooling the solution resulted in the precipitation of unreacted 2-chlorobenzimidazole as white crystalline needles that can be recovered on a sintered glass funnel. The filtrate is then evaporated to dryness and to the oily residue is added anhydrous diethyl ether (50 mL), this precipitate and anhydrous Cs_2CO_3 (219 mg) were placed in a Schlenk tube and methanol (20 ml) was added. The mixture was stirred under an atmosphere of argon at room temperature for two hours. The solvent is then

evaporated under reduced pressure. The residue is extracted with dichloromethane (50 mL), compound **2** is obtained as a yellow crystalline solid (553 mg, 2,2 mmol). Yield: 62 %.

IR (neat ATR Harricks, cm^{-1}): 3420, 3026, 2958, 1632, 1608, 1555, 1497, 1465, 1445, 1393, 1366, 1306, 1267, 1193, 1123, 1104, 1044, 1001, 963, 868, 810, 737, 667, 622, 566, 451, 415.

^{1}H NMR (300.13 MHz, DMSO): δ = 9.86 (d, 2H, ^{2}J = 6.9 Hz, H_{α} pyridynium), 8.16 (d, 2H, ^{2}J = 6.9 Hz, H_{β} pyridynium), 7.48 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_{β} benzimidazol), 6.95 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_{α} benzimidazol), 1.42 (s, 9H, CH_3 *tert*-butyl). $^{13}C\{^{-1}H\}$ NMR (75.47 MHz, DMSO-d_6) δ = 30.0, 36.7, 117.8, 119.9, 125.1, 138.8, 146.9, 170.1.

HRMS - m/z calcd. for $[C_{16}H_{18}N_3+H]^+$ 252.1495; found. 252.1505.

Anal. Calcd. For $C_{16}H_{17}N_3$ (251.33 $g.mol^{-1}$): C, 76.46; H, 4.82; N, 16.72. Found: C, 75.98; H, 6.49; N, 17.15.

Compound 3, 2-4-*N*-pyridinone-1*H*-benzimidazole**:** 2-chlorobenzimidazole (250 mg, 1,64 mmol), with sodium carbonate (190 mg, 0.59 mmol) and anhydrous hydroxypyridine (170 mg, 1,79 mmol) were placed in a Schlenk tube and dimethyl sulfoxide (2 ml) was added. The mixture was heated under an atmosphere of argon at 140 °C for 24h.

The solvent is evaporated under vacuum, and the product is precipitated by addition of 30 ml of DCM. The mixture is then sintered from porosity 4 and then washed with 2x15mL diethyl ether. A brownish solid is obtained (145 mg, 0.64 mmol). Yield: 42%.

IR (neat ATR Harricks, cm^{-1}): 3718, 3276, 2934, 2811, 1638, 1573, 1491, 1417, 1337, 1264, 1178, 1125, 1014, 864, 808, 739, 625, 539, 491, 460, 440.

^{1}H NMR (300.13 MHz, DMSO): δ = 8.46 (d, 2H, ^{2}J = 6.9 Hz, H_{α} pyridone), 7.58 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_{β} benzimidazol), 7.25 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_{α} benzimidazol), 6.39 (d, 2H, ^{2}J = 6.36 Hz, H□ pyridone). $^{13}C\{-^{1}H\}$ NMR (75.47 MHz, DMSO-d_6) □ = 115.5, 118.5, 123.0, 137.0, 138.1, 147.4, 178.9.

HRMS - m/z calcd. for $[C_{12}H_9N_3O+Na]^{+}$ 234.0638, found: 234.0638

Anal. Calcd. For $C_{12}H_9N_3O$ (211.2 $g.mol^{-1}$): C, 68.24; H, 4.29; N, 19.89. Found: C, 68.57; H, 4.13; N, 20.22.

Compound 4, 2-4-tetrafluoroboratopyridinium-1*H*-benzimidazole**:** Potassium pyridine-4-trifluoroborate (365 mg, 1.97 mmol) is added in excess to 2-chlorobenzimidazole (250 mg, 1.64 mmol) in DMSO (2 mL). The mixture is stirred under reflux ($120^{0}C$) overnight. The solvent is evaporated under vacuum, and the product is precipitated by addition of 30

ml of diethyl ether. The mixture is then filtered on sintered porosity is 4 and then washed with 2x15mL Et_2O. A purple-black solid is obtained (407 mg, 1.55 mmol). Yield: 95 %.

IR (neat ATR Harricks, cm^{-1}): 3212, 3119, 2867, 2748, 1626, 1552, 1530, 1500, 1470, 1444, 1415, 1338, 1318, 1263, 1201, 1178, 1112, 1019, 977, 950, 836, 748, 732, 664, 635, 615, 571, 556, 532, 480, 429, 380, 338.

^{1}H NMR (300.13 MHz, DMSO): δ = 9.44 (d, 2H, ^{2}J = 6.9 Hz, H_α pyridynium), 8.18 (d, 2H, ^{2}J = 6.36 Hz, H_β pyridynium); 7.75 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_β benzimidazol), 7.40 (dd, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_α benzimidazol). $^{13}C\{-^{1}H\}$ NMR (75.47 MHz, DMSO-d_6) δ = 116.2, 123.1, 129.9, 137.9, 138.6, 145.9.

HRMS - m/z calcd. for $[C_{12}H_8N_3BF_3\text{-}H]^+$ 262.0771; found: 262.0761.

Anal. Calcd. For $C_{12}H_9BF_3N_3$ (263.0 $g.mol^{-1}$): C, 54.80; H, 3.45; N, 15.98. Found: C, 55.17; H, 3.98; N, 16.31.

Compound 5, 2-4-N,N-dimethylaminopyridiniumbenzimidazole**:** 2-chlorobenzimidazole (250 mg, 1.64 mmol), and 4-dimethylaminopyridine (250 mg, 2.04) were placed in a Schlenk tube and dimethyl sulfoxide (2 ml) was added. The mixture was heated under an atmosphere of argon at

140 °C for 24h. The solvent is evaporated under vacuum, and the product is precipitated by addition of 30 ml of diethyl ether. The mixture is then filtered on sintered porosity is 4 and then washed with 2x15 mL Et_2O. This precipitate and anhydrous Na_2CO_3 (120 mg) were placed in a Schlenk tube and methanol (20 ml) was added. The mixture was stirred under an atmosphere of argon at room temperature for two hours. The solvent is then evaporated under reduced pressure. The residue is extracted with dichloromethane (50 mL). Compound **5** is obtained as a yellow crystalline solid (260 mg, 0.95 mmol). Yield: 58 %.

IR (neat ATR Harricks, cm^{-1}): 1649, 1582, 1536, 1434, 1410, 1270, 1220, 1125, 1103, 1004, 955. 817, 750, 628, 537, 495, 446, 366, 306.

^1H NMR (300.13 MHz, DMSO): δ = 9.24 (d, 2H, ^2J = 6.9 Hz, H_α pyridynium), 7.37 (dd, 2H, ^2J = 9.0 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz, H_β benzimidazol), 7.13 (d, 2H, ^2J = 6.4 Hz, H_β pyridynium), 6.85 (dd, 2H, ^2J = 9.0 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz, H_α benzimidazol), 3.28 (s, 6H, CH_3 pyridynium). $^{13}C\{^{-1}H\}$ NMR (75.47 MHz, DMSO-d_6) δ = 40.4, 107.8, 115.5, 122.6, 137.6, 138.5, 146.7, 156.7.

HRMS - m/z calcd. For: $[C_{14}H_{15}N_{4+}H]^+$ 239.1291; calc. 239.1295.

Anal. Calcd. For $C_{14}H_{14}N_4$ (238.3 $g.mol^{-1}$): C, 70.57; H, 5.92; N, 23.51. Found: C, 70.05; H, 6.07; N, 23.79.

Compound 6, 2-pyridiniumpyrimidine bromide**:** 2-bromopyrimidine (250 mg, 1.58 mmol) and anhydrous pyridine (0.15 mL) were placed in a Schlenk tube and dimethyl sulfoxide (2 ml) was added. The mixture was refluxed under an atmosphere of argon at 120 °C for 24h. The solvent is evaporated under vacuum, and the product is precipitated by addition of 30 ml of diethyl ether. The mixture is then filtered on sintered porosity is 4 and then washed with diethylether (2x15mL). Compound **6** is obtained as a dark crystalline solid (370 mg, 1.56 mmol). Yield: 99 %.

IR (neat ATR Harricks, cm^{-1}): 3129, 3041, 2990, 1624, 1592, 1560, 1481, 1451, 1407, 1286, 1193, 1041, 996, 858, 808, 772, 674, 648,627, 493.

^{1}H NMR (300.13 MHz, CD_3CN): δ = 10.00 (dd, 2H, ^{2}J = 6.9 Hz, H_α pyridynium), 9.12 (d, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_α pyrimidine), 8.87 (tt, 2H, H_β pyridynium), 8.33 (t, 1H, H_β pyrimidyne), 7.88 (t, 1H, H_δ pyrimidine). $^{13}C\{-^{1}H\}$ NMR (75.47 MHz, DMSO-d_6) δ = 124.4, 128.5, 141.7, 150.7, 160.9.

HRMS - m/z calcd. for: $[C_9H_8N_3]^+$ 158.0713, found: 158.0712

Anal. Calcd. For $C_9H_8BrN_3$ (238.1 $g.mol^{-1}$): C, 45.40; H, 3.39; N, 17.65. Found: C, 45.91; H, 3.88; N, 18.03.

Compound 7, 2-4-*tert*-butylpyridiniumpyrimidine bromide**:** 2-bromopyrimidine (1 g, 6.3 mmol) and anhydrous 4-tert-butylpyridyl (1.5 mL) were placed in a Schlenk tube and acetonitrile (20 ml) was added. The mixture was refluxed under an atmosphere of argon at 100 °C for 48h. The solvent is evaporated under vacuum, and the product is precipitated by addition of 30 ml of diethyl ether. The mixture is then filtered on sintered porosity is 4 and then washed with 2x15mL diethylether. Compound **7** is obtained as a white crystalline solid (1.3 g, 4.43 mmol). Yield: 68 %.

IR (neat ATR Harricks, cm^{-1}): 3012, 2964, 1634, 1590, 1556, 1499, 1437, 1402, 1370, 1291, 1205, 1127, 1109, 1094, 1054, 994, 841, 789, 739, 708, 663, 630, 574, 518, 489, 448.

^{1}H NMR (300.13 MHz, DMSO): δ = 9.88 (d, 2H, ^{2}J = 6.9 Hz, H_α pyridynium), 9.23 (d, 2H, ^{2}J = 9.0 Hz, H_α pyrimidine), 8.40 (d, 2H, ^{2}J = 6.9 Hz, H_β pyridynium), 7.98 (t, 1H, H_β pyrimidine), 1.46 (s, 9H, CH_3 *tert*-butyl). ^{13}C{-^{1}H} NMR (75.47 MHz, DMSO-d_6) δ = 207.2, 175.5, 160.8, 155.8, 140.9, 125.4, 124.2, 37.4, 30.3.

HRMS - m/z calcd. for $[C_{13}H_{16}N_3]^+$ 214.1347; found. 214.1339.

Anal. Calcd. For $C_{13}H_{16}BrN_3$ (294.2 $g.mol^{-1}$): C, 53.07; H, 5.48; N, 14.28. Found: C, 52.79; H, 5.18; N, 14.81.

Compound 8, 2-4-*N*-pyridinonepyrimidine**:** 2-bromopyrimidine (250 mg, 1,58 mmol), with sodium carbonate (160mg) and anhydrous hydroxypyridine (150 mg, 1.1eq) were placed in a Schlenk tube and dimethyl sulfoxide (2 ml) was added. The mixture was refluxed under an atmosphere of argon at 140 °C for 24h. The solvent is evaporated under vacuum, and the product is precipitated by addition of 30 ml of dichloromethane. The mixture is then sintered from porosity 4 and then washed with 2x15mL Et_2O. A black purple solid is obtained (210 mg, 1,21 mmol).

Yield: 77 %.

IR (neat ATR Harricks, cm^{-1}): 3081, 1634, 1593, 1578, 1565, 1545, 1436, 1395, 1347, 1314, 1183, 1104, 1084, 1040, 849, 830, 791, 721, 649, 627, 585, 538, 451, 418, 375, 321.

^{1}H NMR (300.13 MHz, DMSO): δ = 9.02 (d, 2H, ^{2}J = 6.9 Hz, H_α pyridynium), 8.96 (d, 2H, ^{2}J = 9.0 Hz, $^{3}J_{H\text{-}H}$ = 2.7 Hz, H_α pyrimidyne),), 7.60 (t, 1H, H_β pyrimidyne), 6.60 (d, 2H, ^{2}J = 6.9 Hz, H_β pyridynium). $^{13}C\{\text{-}^{1}H\}$ NMR (75.47 MHz, DMSO-d_6) δ = 178.1, 159.6, 154.9, 136.8, 120.2, 117.0,

HRMS - m/z calcd. for $[C_9H_7N_3O+Na]^+$ 196.0481, found: 196.0483.

Anal. Calcd. For $C_9H_7N_3O$ (173.2 g.mol^{-1}): C, 62.42; H, 4.07; N, 24.27. Found: C, 62.91; H, 3.95; N, 24.69.

Compound 9, 2-4-tetrafluoroboratopyridiniumpyrimidine**:** Potassium pyridine-4-trifluoroborate (322 mg, 1.74) is added in excess to 2-bromopyrimidine (250 mg, 1.58 mmol) in DMSO (2 mL). The mixture is stirred under reflux (120^{0}C) overnight. The solvent is evaporated under vacuum, and the product is precipitated by addition of 30 ml of diethyl ether. The mixture is then filtered on sintered porosity is 4 and then washed with 2x15mL Et_2O. A black solid is obtained (316 mg, 1.40 mmol).

Yield: 89 %.

IR (neat ATR Harricks, cm^{-1}): 2921, 1630, 1592, 1562, 1405, 1282, 1187, 1015, 955, 854, 823, 788, 620, 504, 419, 325.

^{1}H NMR (300.13 MHz, DMSO-d_6): δ =9.71 (d, 2H, ^2J = 6.9 Hz, H_α pyridynium), 9.20 (d, 2H, ^2J = 9.0 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz, H_α pyrimidyne), 8.18 (d, 2H, ^2J = 6.9 Hz, H_β pyridynium), 7.92 (t, 1H, H_β pyrimidyne). ^{13}C{-^{1}H} NMR (75.47 MHz, DMSO-d_6) δ = 123.97, 130.34, 138.19, 155.70, 160.69.

HRMS ESI- m/z calcd. for $[C_9H_7N_3BF_3+ K]^+$ 264.0316; found: 264.0318.

Anal. Calcd. For $C_9H_7BF_3N_3$ (225.0 g.mol^{-1}): C, 48.05; H, 3.14; N, 18.68. Found: C, 48.47; H, 2.98; N, 19.01.

Compound 10, 2-4-N,N-dimethylaminopyridiniumpyrimidine bromide**:** 2-bromopyrimidine (250 mg, 1.56 mmol) and 4-dimethylaminopyridine (382 mg, 3.13 mmol) were placed in a Schlenk tube and acetonitrile (20 ml) was added. The mixture was refluxed under an atmosphere of argon at 100 °C for 48h. The solvent is evaporated under vacuum, and the product is precipitated by addition of 30 ml of diethyl ether. The mixture is then filtered and washed with 2x15mL Et2O. Compound **10** is obtained as a whit crystalline solid (214mg, 0.765 mmol).

Yield: 49 %.

IR (neat ATR Harricks, cm^{-1}): 3447, 3407, 3072, 1641, 1580, 1560, 1439, 1409, 1385, 1343, 1327, 1306, 1225, 1195, 1089, 1047, 941, 830, 787, 725, 662, 630, 574, 536, 516, 479, 446.

^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 9.21 (d, 2H, ^2J = 6.9 Hz, H_α pyridynium), 9.06 (d, 2H, ^2J = 9.0 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz, H_α pyrimidyne), 7.74 (t, 1H, H_β pyrimidyne), 7.28 (d, 2H, ^2J = 6.9 Hz, H_β pyridynium), 3.40 (s, 6H, CH_3 methyl). ^{13}C{-^{1}H} NMR (75.47 MHz, DMSO-d_6) δ = 41.0, 108.3, 121.9, 137.2, 154.9, 158.0, 160.3.

HRMS - m/z calcd. for $[C_{11}H_{13}N_4]^+$ 201.1140; found: 201.1135.

Anal. Calcd. For $C_{11}H_{13}N_4$ (281.1 $g.mol^{-1}$): C, 46.99; H, 4.66; N, 19.93. Found: C, 45.43; H, 4.25; N, 20.27.

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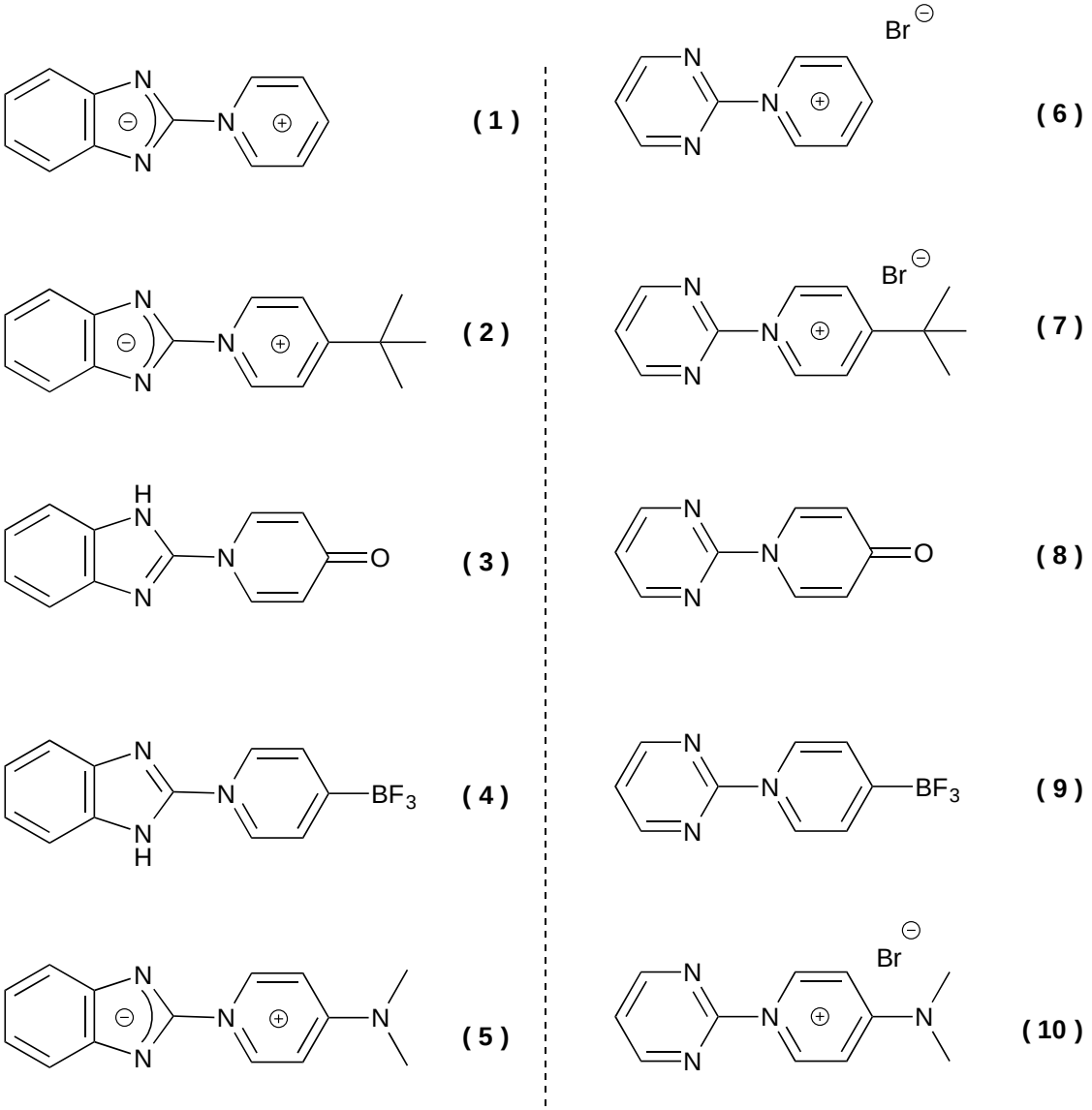
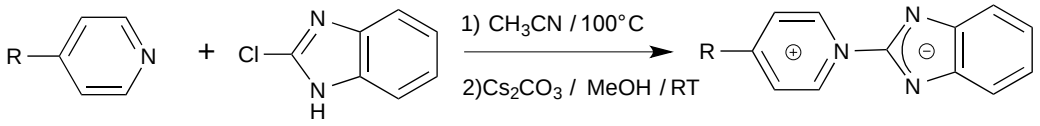
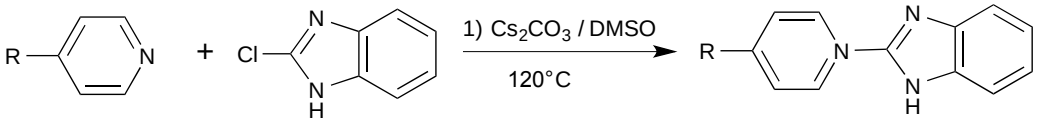


Figure 1: Novel pyridinium-benzimidazole and pyridinium-pyrimidine scaffolds.

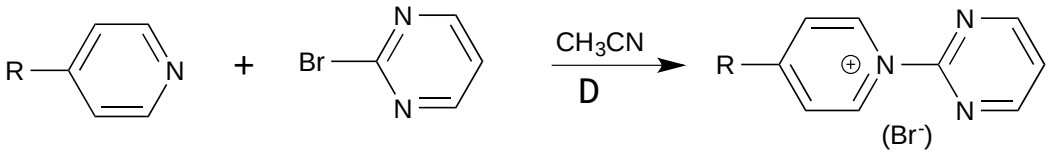


R = -H, t-Bu, NMe_2 R = -H (**1**), -t-Bu(**2**), -NMe_2 (**5**)

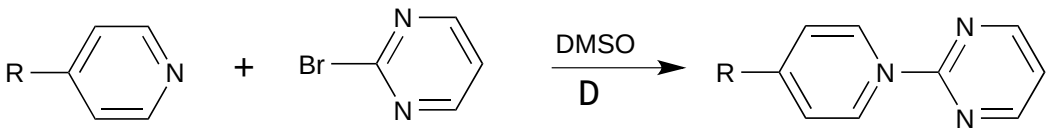


R = -OH, -BF_3- R = -O (**3**), -BF_3 (**4**)

Scheme 1: Synthesis of the pyridinium-betaine molecules with the benzimidazole core (**1-5**)



R = -H, t-Bu, NMe_2 R = -H (**6**), -t-Bu(**7**), -NMe_2 (**10**)



R = -OH (+ Na_2CO_3), -BF_3^- R = =O (**8**), -BF_3^- (**9**)

Scheme 2: Synthetic routes to the novel compounds **6-10** based on the pyrimidine core

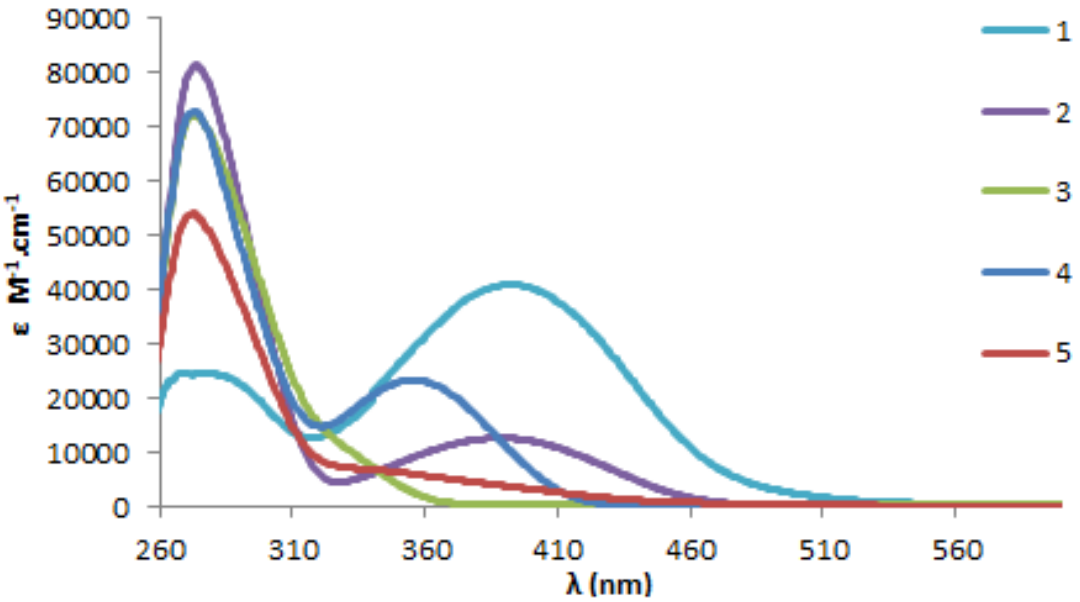


Figure 2: Absorption spectra of compounds **1-5** in acetonitrile

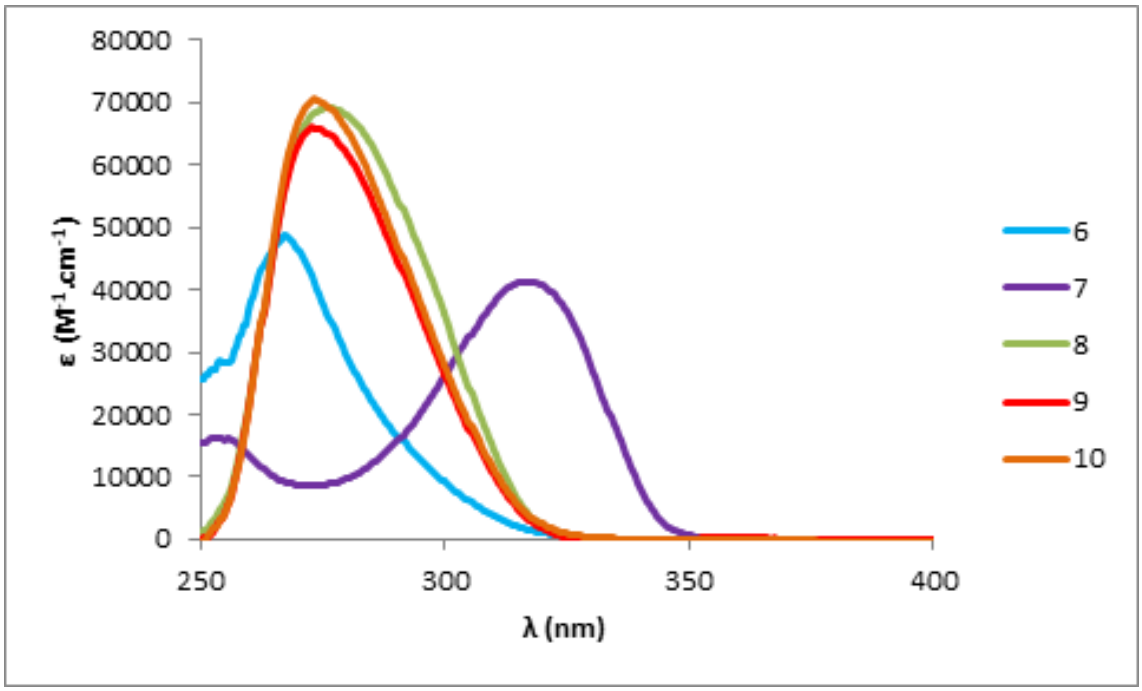


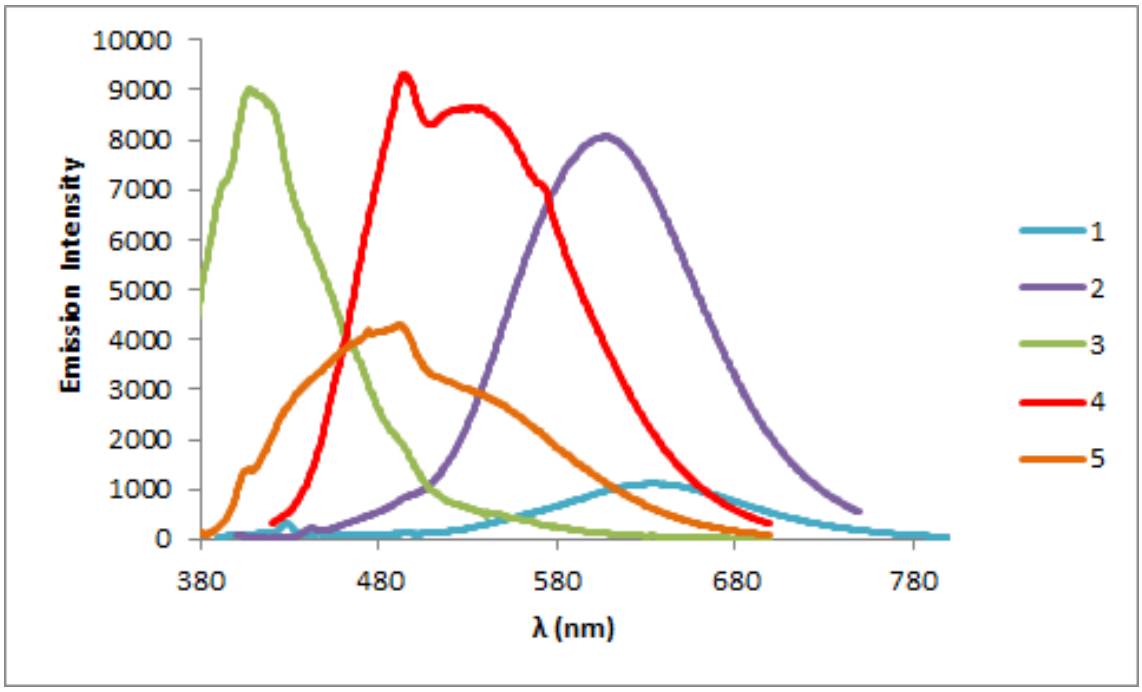
Figure 3: Absorption spectra of compounds **6-10** in acetonitrile

Table 1: UV-Vis. absorption data for compounds **1-10**

	λ_{abs} (nm)	ε ($mol^{-1}.L.cm^{-1}$)x10^4
1	269; 392	2.47; 4.09
2	273; 388	8.11; 1.27

3	273	7.21
4	273; 355	7.29; 2.34
5	272	5.39
6	267	4.87
7	317	4.13
8	277	6.91
9	273	6.59
10	273	7.04

1



2

3 **Figure 4:** Photoluminescence spectra of compounds **1-5** in air equilibrated

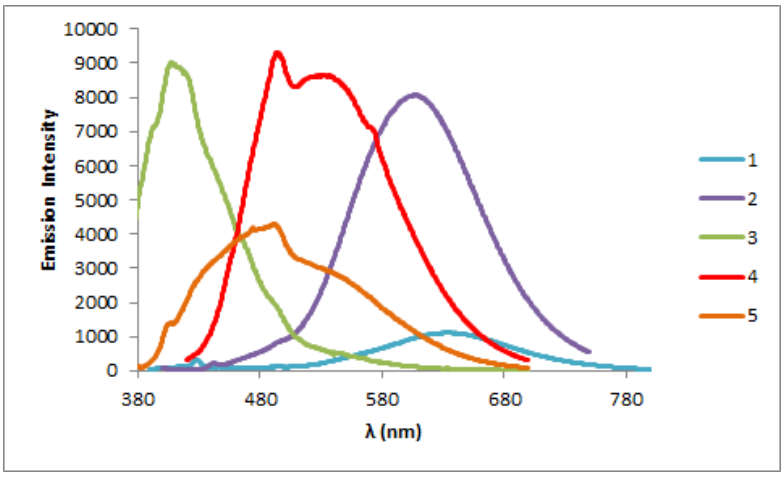
4 dichloromethane solutions.

5

6

1 Graphical abstract

2 A series of pyridinium-betaine like molecules has been reported. The title
3 compounds were prepared by mixing 2-chlorobenzimidazole or 2-
4 bromopyrimidine with the corresponding pyridines (pyridine, 4-*tert*-
5 butylpyridine, 4-hydroxypyridine, potassium 4-trifluoroboratepyridine, 4-
6 dimethylaminopyridine). Preliminary photoluminescence results showed
7 that some of the compounds could behave as single-component
8 panchromatic emitters.



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