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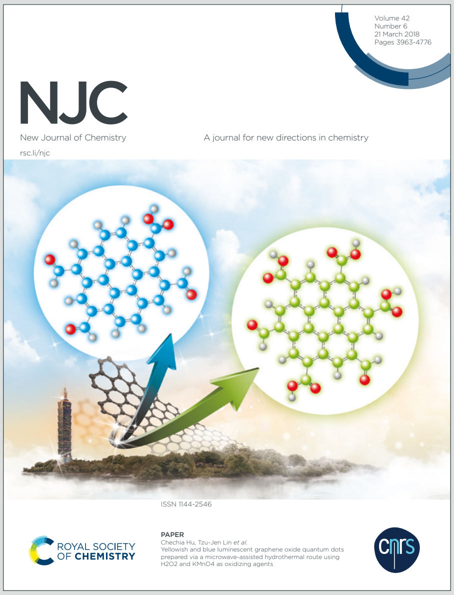

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PAPER
Chechia Hu, Tzu-Jen Lin *et al.*
Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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ARTICLE

Poly-halogenated aza-bodipy dyes with improved solubility as versatile synthetic platform for the design of photonic materials.

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The optimization of the solubility in organic solvents of halogenated aza-dipyrromethenes was achieved by substitutions of the upper phenyl moities by branched long alkoxy (**1f**) or by using a OMe-OHex-OMe pattern (**1h**). These results allowed us to prepare original tetra-halogenated aza-dipyrromethenes that were used as synthetic platforms to access highly functionalized aza-bodipy dyes for various potential applications including PDT, imaging, or nonlinear optics.

Introduction

Aza-bodipy dyes whose characteristic architecture is depicted Figure 1, are a versatile class of chromophore featuring strongly red-shifted absorption and high extinction coefficient that became very popular following pioneering works of O'Shea's group in the early 00's.[1,2] Their particular photophysical properties have been extensively studied for a wide range of applications: (i) in biology, either for fluorescence[3] and photoacoustic imaging[4] or photothermal[5] and photodynamic therapy[2a,6] or sensing;[7] (ii) in material sciences for organic electronics and photonics (e.g. photovoltaics, nonlinear optics (NLO), optical power limitation (OPL)…).[8]

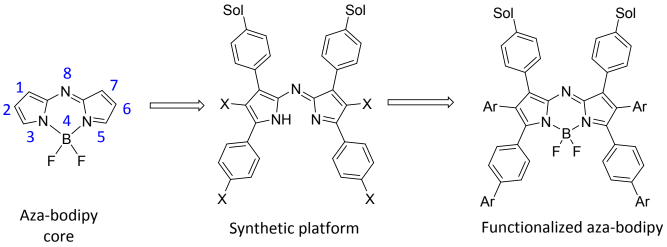

Figure 1. General structure of aza-bodipy core and poly-halogenated aza-dipyrromethene intermediate for the access to highly functionalized dyes.

The main reason for the enthusiasm for this class of dyes lies on their versatile structure featuring different functionalization positions, their important chemical and electrochemical stability and their intense absorption bands that can be tuned by the substitution and shifted in the red- or infrared spectral range.[9] From a synthetic point of view, the preparation of these functional chromophores generally requires a multistep procedure with intermediates featuring reactive groups like halogens (Br, I) for further cross-coupling reactions.[8c,9b,10] However, whereas the aza-bodipy dyes present generally an acceptable solubility in most of the common organic solvents, their aza-dipyrromethene precursors, and particularly bis- or tetra-halogenated intermediates present a really poor solubility leading to difficult purification steps and product characterization, limited reactivity, resulting in poor yields in the case of multi-steps synthesis (Figure 1).[11] Solubility improvements are generally intended by addition of alkyl substituents but rational reports concerning this aspect are really scarce in the literature[12] and completely absent for aza-bodipy dyes. In this context, we decided to carry out a systematic solubility improvement study on one di-bromo-aza-dipyrromethene intermediate (**1a**) involved in advanced functional dye synthesis. **1a** presents a modest solubility in common organic solvents and its further halogenation attempts were described as almost impossible due to the insolubility of the reaction products.[11a] Introduction of two *m*-OMe groups reported by Ramaiah et al. enabled the preparation of polyhalogenated compounds but the solubility was still not optimized.[13] In this article, we report the synthesis of a series of analogous of **1a** where the phenyl fragments located at the upper positions (positions 1,7) were further substituted by alkyl groups (e.g. -*ter*-butyl (**1b**)), by linear or branched alkoxides (e.g. hexyloxy (**1c**), nonan-5-yloxy (**1d**), (2-ethylhexyl)oxy, (**1e**), (2-hexyldecyl)oxy (**1f**)) or by three *meta* and *para* alkoxides (eg. tris-methoxy (**1g**), bis-methoxy, hexyloxy (**1h**)) as depicted in **Figure 2**. The maximal solubility in THF was determined and the most soluble compounds **1f,h** were used as synthetic platforms for the preparation of polyhalogenated derivatives or advanced functional dyes featuring extended conjugated backbone. In this latter case, the functionalized

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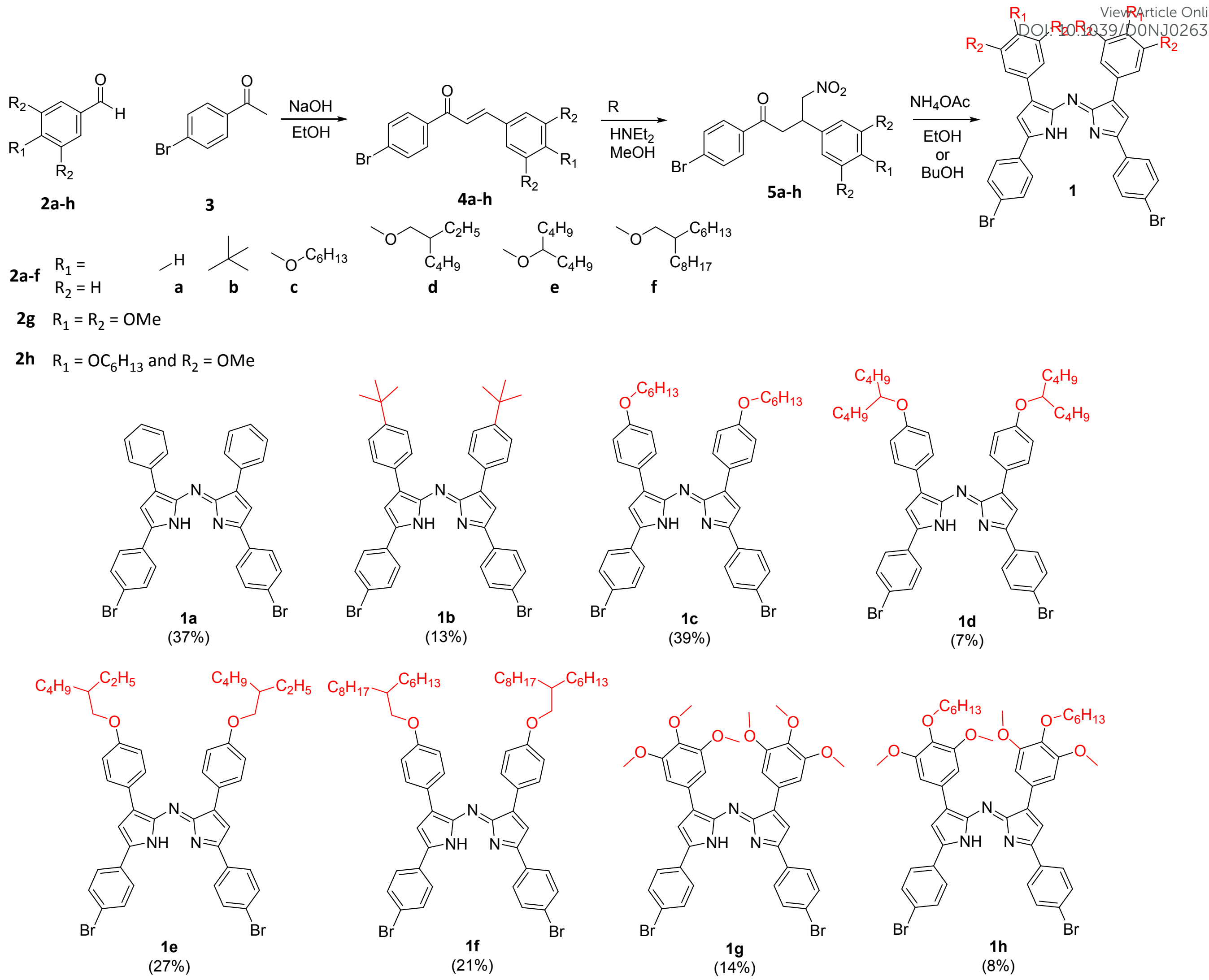

Figure 2. Reference aza-dipyrromethene **1a** and compounds **1b-h** studied for solubility improvement. In red are indicated the nature of the solubilizing substituents. In the upper part of the figure is represented the classical synthetic scheme. Brackets correspond to global yields over 3 steps.

aza-bodipy dyes can be used as pure material for thin film preparation using spin coating technique or pure material by simple melting.

Results and discussion

Synthetic procedures. The synthesis of the aza-dipyrromethene (**1a-h**) was achieved using the classical three steps synthetic procedure involving (i) the aldol condensation of the desired aldehyde with 4'-bromoacetophenone, (ii) the Michael addition of nitromethane and (iii) the final cyclisation/condensation step leading to aza-dipyrromethenes (**1a-h**) in the presence of ammonium acetate in refluxing ethanol or butanol.[2a] All compounds were purified by precipitation or chromatography and characterized by ^{1}H NMR and mass spectrometry (see SI for details).

Crystallography. Interestingly, in the case of **1d** and **1g**, crystals suitable for X-ray structure determination were obtained by slow diffusion of dichloromethane in ethanol at RT. Structures are depicted in Figures 3 and 4 and crystallographic data, refinement parameters and selected bonds lengths and angles are compiled in Tables S1 and S2. It is worth noting that many crystal structures of aza-bodipy dyes are described in the literature,[2,8,9] structures of aza-dipyrromethene precursors are less common. In both cases, the aza-dipyrromethene structures are very similar; they adopt the expected *cisoid* conformation with a very planar structure and classical bond distances (Table S2). Due to the larger steric hindrance of **1d** compared to **1g**, the crystal packing and molecular arrangement are different (Figure 4). In the *a*-direction of the unit-cell, molecules of **1d** are organized in a head-to-tail way. Due to the upper site volume, molecules are offset from each other along the *b*-axis of the unit-cell. Then, the crystal packing of these molecules can be viewed as waves running along the *c*-axis of the unit-cell stacking on top of each other along the *b*-axis of the unit-cell. In case of **1g**, volume of the upper site of the molecule is smaller and molecules stack perfectly on the top each other along the *a*-axis of the unit-cell forming planes. Each plane is separated from its neighbour by co-crystallized THF solvent molecules.

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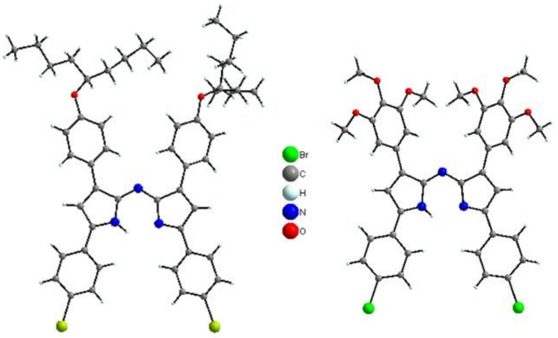

Figure 3. Crystal structures **1d** (left) and **1g** (right).

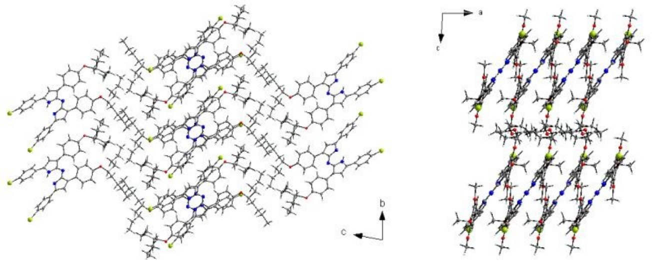

Figure 4. Crystal packing of **1d** (left) and **1g** (right) along the *a*-axis and *b*-axis of the unit-cell, respectively.

Solubility measurements. The solubility determination was performed using a method inspired by that of Hill et al. used in the case of perylene diimide dyes.[12] At first, the absorption spectra were measured (Figure 5) and the extinction coefficients were carefully determined using a Beer-Lambert Law method (Table 1). All compounds present rather similar absorption profile with an intense and broad band around 610 nm. One can notice that introduction of alkoxy fragment slightly red-shifts the absorption maxima compared to **1a,b**. Then, a saturated THF solution was prepared at room temperature and filtered off, the filtrate was diluted and the saturation concentration (C_{sat}) was determined by comparison of the diluted solution absorption with a calibration curve previously established for all compounds (see SI for details, Figure S2). The experimental protocol was tested several time on **1a** to evaluate the experimental error. The calibration was made twice (Figure S3) and very similar slopes were found; the error can be estimated to 2% mainly due to weighing imprecision. Then five different THF saturated solutions have been prepared leading to an average C_{sat} (**1a**) value of 7.6 ± 0.6 mg.mL^{-1} (Table S3). The uncertainty of the measure is of about 10%, of course higher than that of the calibration curve and may be explained by room temperature variation over a large period of time. This protocol was then applied for all aza-dipyrromethenes (**1b-h**) and the results are compiled in the Table 1. For comparison, we defined the solubility enhancement ratio (R^S) as the ratio of the sample's saturation concentration to the saturation concentration of the reference **1a** (the values are taken in mmol.L^{-1}).

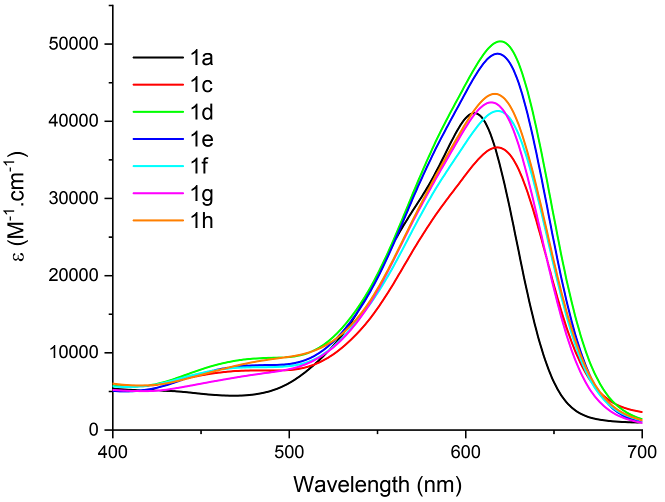

Figure 5. UV-visible absorption spectra of compounds **1a-h** in THF.

Table 1. Saturation concentration measurements in THF at room temperature.

	λ_{max} [nm]	ε [M^{-1}.cm^{-1}]	C_{sat} ^{a} [mmol.L^{-1}]	C_{sat} ^{a} [mg.mL^{-1}]	$R^{S\ b}$
1a	605	41000	13	8	1
1b	606	-^{c}	-^{c}	-^{c}	-^{c}
1c	618	37000	19	15	1.5
1d	620	51000	81	72	6.4
1e	617	49000	43	37	3.4
1f	618	41000	101	110	8.0
1g	614	43000	4	3	0.3
1h	616	44000	>124^{d}	>115^{d}	>9.9^{d}

a : values given with 10% error, b : for a compound X, $R^s(X) = C_{sat}(X)/C_{sat}(1a)$ with the saturation concentration in mmol.L^{-1}. c: not soluble enough. d: saturation concentration not reached.

Tetra-halogenated platforms. The high increase in aza-dipyrromethene intermediates solubility is of great interest for further functionalization of aza-bodipy dyes. Indeed, with the modification made on upper 1,7 positions, it is now possible to halogenate directly side 2,6 positions, to obtain tetra-halogenated aza-dipyrromethenes. Using most soluble compounds **1f** and **1h**, several examples of bromination or iodination of the 2,6 positions have been prepared in good yields by reaction with bromo-or iodo-succinimide respectively and are listed in Figure 6. Tetra-halogenated aza-dipyrromethenes **6**-**9** present good solubility in common organic solvents and are the first to be fully characterized by NMR (see SI for details). These compounds could be used as a synthetic platform for orthogonal palladium catalyzed cross-coupling reactions or to prepare corresponding tetra-halogenated aza-bodipy dyes. As an example, molecule **10** was synthesized by successive iodination and borylation of intermediate **1f** with an 86% yield. This molecule presents also an excellent solubility and was fully characterized. Spectroscopic data obtained on molecule **10** are shown Figure 7 and Table 2. This dye presents a sharp and intense absorption band (λ = 660 nm, ε = 71500 L.mol^{-1}.cm^{-1}) with a slight shouldering around λ =

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560 nm, which is characteristic of aza-bodipy dyes having a strong cyanine transition character. Fluorescence measurements have been conducted in DCM and showed a narrow mirror emission band centered on 723 nm with a negligible quantum yield $\phi < 0.01$. This very weak fluorescence could be explained by the presence of heavy atoms favoring intersystem crossing and population of the triplet state via spin-orbit coupling enhancement.[11b] Singlet oxygen generation of molecule **10** in DCM was evaluated by measuring phosphorescence at 1270 nm, using phenalenone as a reference. As expected, aza-bodipy **10** presents a high singlet oxygen generation quantum yield $\phi_\Delta = 0.58$ which confirms previous observations by Adarsh et al. on analogous compounds.[13] As future perspective, the tetrahalogenated compounds presented here can have interesting properties for PDT or photo-acoustic imaging.[4,6,13,14]

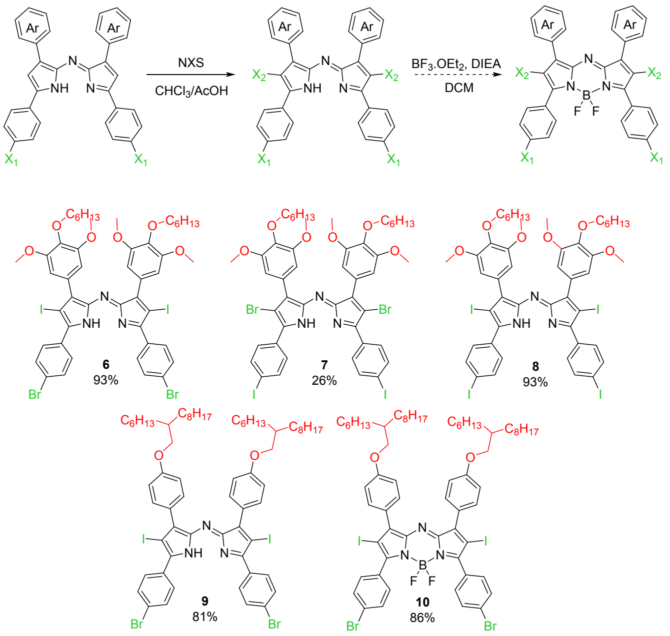

Figure 6. Synthesis of tetra-halogenated aza-dipyrromethenes and corresponding aza-bodipy dyes.

Advanced photonic dyes. The second application of these improved solubility aza-bodipy concerned the synthesis of advanced chromophore for photonics and more precisely the design of molecular materials for optical power limitation (OPL), *i.e.* the protection of optical devices or eyes against incident laser threats.[15] In this context, organic dyes featuring optimized nonlinear optical properties are particularly appealing but required to be used in extremely high concentration either in solution or as a guest in materials. In the last decade, our group reported the aza-bodipy dye **12a**, functionalized at the 1,7 positions by dihexylaminophenylethynyl chromophore (Figure 8) which consist in the benchmark chromophore for optical protection at telecommunication wavelength (1550 nm) in solution or in sol-gel material.[16] In order to further improve the solubility of this chromophore in organic solvents, we decided to prepare analogous dyes, **11f** and **11h** further functionalized at the top positions (1,7) by the best solubilizing moieties. The aza-dipyrromethenes **1f** and the

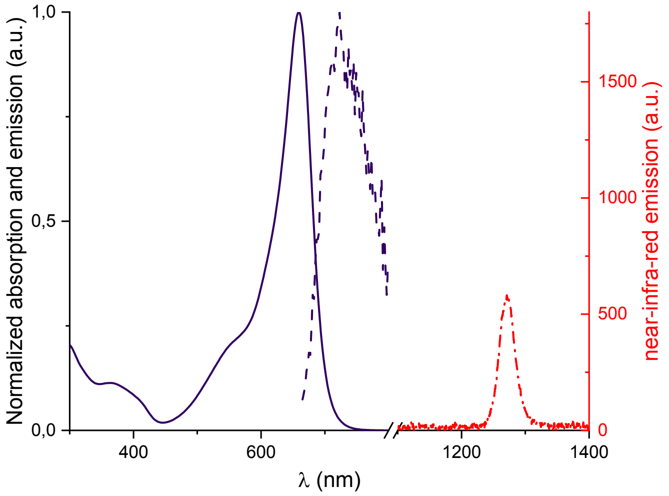

Figure 7. Absorption (blue line) and emission (dashed blue line) spectra of compound **10** in DCM. In red is represented the emission of singlet oxgen observed after irradiation of **10** (λ_{ex} = 600 nm).

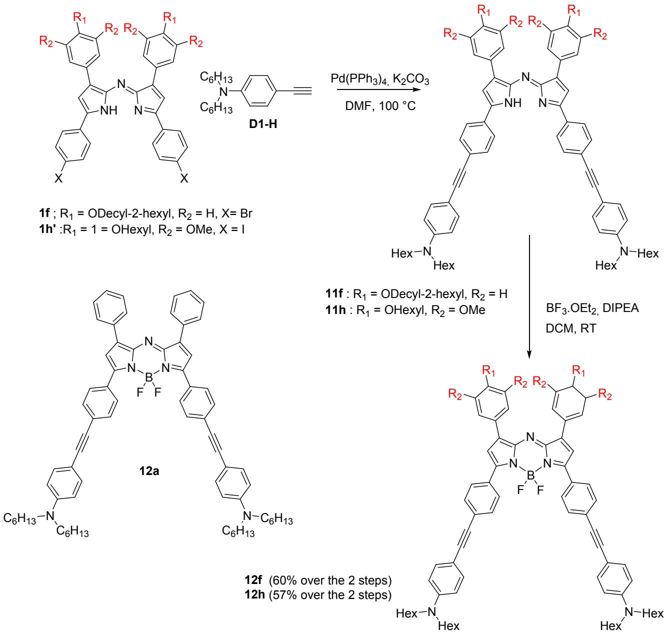

Figure 8. Structure of the benchmark dye **12a** used for optical limitation at 1500 nm and synthetic scheme for the preparation of **12f,h**.

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more reactive analogous **1h'** featuring para-iodo substituents have been further involved in a Pd-Catalysed Sonogashira cross-coupling. Classical conditions involving $PdCl_2(PPh_3)_2/CuI$ mainly led to the formation of the Glaser type homocoupling product. The reaction was optimized and copper free conditions were found using $Pd(Ph_3)_4$ as a catalyst in DMF at 100°C in the presence of potassium carbonate gave the best yield of formation of the desired product that was immediately involved in the borylation step without purification. The global yield after chromatography for this two-steps procedure was 57 % and 60% for **12h** and **12f** respectively and both compounds were fully characterized (see SI). Importantly these last compounds present almost identical absorption properties than the benchmark molecule in dichloromethane solution (Figure 9 and Table 2) with a minor shift of the main absorption band (Δλ = -4 nm and +5 nm for **12f** and **12h,** respectively). The emission behaviours of **12f,h** are also very similar to **12a** with a luminescence quenching in polar solvent like dichloromethane and a significant emission above 800 nm in apolar solvent like toluene (Table 2). One can notice an increase in emission quantum yield and lifetime in the case of compound **12f**.

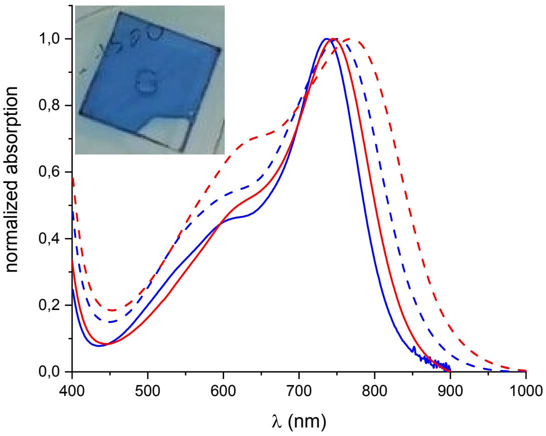

Figure 9. Normalized absorption spectra of **12f** (blue) and **12h** (red) in diluted dichloromethane solution (full lines) and thin films (dotted lines). In inset is reported a picture of the pure molecular thins film obtained by spin-coating of **12h**.

Table 2. Photophysical properties of aza-bodipy dyes **10**, **12a** and **12f,h** in dichloromethane at room temperature.

compound	λ_{max} [nm]	ε [L. mol^{-1}.cm^{-1}]	λ_{em} [nm]	ϕ^a	τ [ns]	ϕ_Δ^b
10	660	71500	723	<0.01	-	0.58
12a	740	57 000	825^a	0.04	0.7	-
12f	736	65 000	807^a	0.11	1.4	-
12h	745	50 000	824^a	0.05	0.7	-

a : measurment in toluene, (H/OMe)BF_2 was used as a reference[11] (ϕ = 0.36 dans le $CHCl_3$). b : phenalenone was used as a reference (ϕ_Δ = 96 % dans le DCM).

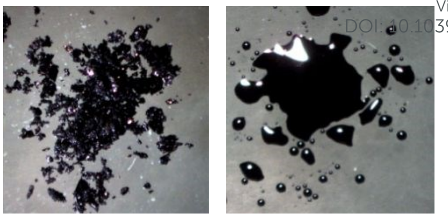

Figure 10. Solid amorphous powder of compound 12h (left) and glassy solid obtained after successive heating and cooling (right).

However, the most important modification concerns the morphological aspect of the dyes: whereas **12a** can be isolated as a microcrystalline powder, **12f** is a wax and **12h** is an amorphous powder that becomes a glass after low temperature melting (< 60°C). As a consequence, these two last molecules formed easily pure molecular thin films by drop-casting or spin coating from a concentrated chloroform solution, which was not the case for **12a** (Figure 9). The absorption spectra of these material were measured. For both molecules, a broadening of absorption spectra was observed, typical behavior for pure molecular films on a surface,[17] as well as an increase in relative intensity of the higher energy absorption band around 600 nm compared to the main absorption peak. Finally, the facility of the processing of these new molecules will allow the preparation of thick pure molecular films or materials similar to those prepared by Weder and coworkers[18] for several application including nonlinear optics. Indeed, molecule **12h** can be melted by gentle heating and transfer into a mold. By simply cooling to RT, **12h** forms a glassy solid (Figure 10) which is currently investigated as material for optical power limiting applications.

Conclusions

In this paper, we presented new halogenated aza-dipyrromethenes and we studied their solubility in common organic solvents, in particular THF. The substitutions of the upper phenyl moieties by branched long alkoxy (**1f**) or by using a OMe-OHex-OMe pattern (**1h**) were identified as greatly increasing the solubility compared to the non-substituted reference molecule **1a** by a factor around 10. This solubility improvement allowed the easy preparation of tetra-halogenated aza-dipyrromethene which were up to now not fully described in the literature because of their lack of solubility in organic solvents. These molecules are useful as synthetic platform to access highly functionalized aza-bodipy dyes for various potential application including PDT, imaging, or nonlinear optics. For this latter application two new dyes bearing the most solubilizing groups have been prepared by grafting an electron donating group. These chromophores are analogues to benchmark short-wave infrared OPL dye but presented very interesting physical properties including low melting point, high filmability which paves the way for pure processing opportunities and for the design of thick films or melt processed materials for OPL.

Conflicts of interest

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There are no conflicts to declare.

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