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Efficient synthesis of solid-emissive Boron-Fluorine derivatives

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ABSTRACT

A highly solid-emissive Boron–Fluorine scaffold with two conjugated alkyne groups (**BOPIM-S**) is facilely synthesized, which shows enhanced fluorescent intensity compared to the BOPIM dye without alkyne units. According to X-ray single crystal analysis, the terminal alkyne groups interact with atoms B, F, C and N on neighbouring molecules, producing a rigid rectangular structure, which helps to avoid energy loss via non-irradiative decay. Furthermore, **BOPIM-S** can undergo copper catalysed alkyne–azide-cyclo-addition (CuAAC) chemistry with aromatic azides to produce conjugated molecules with high yields. According to absorption and fluorescent measurements, all these compounds synthesized by CuAAC emit large Stokes shift (over 100 nm) both in solution and in solid state. But the electronic environments of terminal aromatic rings slightly affect their photophysical properties.

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Interest in solid-emissive dyes is still ongoing, as they have a wide range of potential applications in optoelectronic devices, sensors and light harvesting system.¹ Although a large number of chromophores exhibit excellent fluorescent property in dilute solutions, examples of solid-emissive dyes are limited because most of them tend to aggregate in concentrated solution or in solid state. A lot of factors may cause severe concentration-induced fluorescence quenching, such as torsional induced non-radiative deactivation, presence of traps or dopants and most importantly planeto-plane stacking-induced intermolecular coupling of electronic transition dipole moments.² To avoid these limitations, some strategies have been proved to be effective, such as introducing bulky steric groups,³ constructing non-covalent bonds to promote nonparallel packing etc. Among all the chromophores developed till now, we are most interested in Boron-Fluorine derivatives, because of their large number of advantages over other dyes, namely high fluorescence quantum yield and large absorption coefficient, excellent chemical- and photochemical-stability, long excitedstate lifetimes, a large two-photo cross-section, good solubility and narrow emissive band. In order to solve the problem of concentration-induced fluorescence quenching, heterocyclic rings can be adopted instead of pyrrole to construct intermolecular non-covalent bonds, which would result in non-parallel packing in solid state.⁴ Previously, we developed such a class of solid-emissive Boron-Fluorine dyes (BOPIM), using 2-(2'-pyridyl) imidazole derivatives as ligands.⁵ This class of dyes exhibit high fluorescent intensity in solution, amorphous solid film and crystal state. And the dyes' Stokes shifts are highly enlarged compared to typical

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0040-4039/\$ - see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tetlet.2013.05.116 BODIPY dyes (normally over 100 nm), due to the intramolecular charge transfer (ICT) from electron-rich groups to electron-deficient boron centre. We also found that the terminal groups conjugated to the imidazoles play important roles in determining BOPIMs' photophysical properties. For example, when terminal groups are halogen atoms or methoxyl moieties which can easily form intermolecular non-covalent bonds, they show comparatively high fluorescence quantum yields both in solution and in solid state.^{5b-d} If the terminal groups are fluorescence quenching groups (like nitro), or torsional moieties (N,N'-dimethylamino) with TICT characteristic, very low or no fluorescence were observed in solution or amorphous powder.^{5e} BOPIM dyes' emission wavelength is also tunable by conjugating electron donors or acceptors to the BOPIM skeleton.^{5c} But all the BOPIM dyes reported so far are synthesized from original starting materials. Therefore, it is necessary to develop a more straightforward method to synthesize solidemissive BOPIM dyes from a simple intermediate under mild reaction conditions. And conjugated structures are preferred, because their photophysical properties are highly related to conjugation. Based on the above considerations, we describe here the synthesis and characterizations of a novel solid-emissive BOPIM scaffold with conjugated alkyne groups (BOPIM-S), and use it as a core scaffold to react with different aromatic azides to provide various conjugated structures (see Scheme 1).

Synthesis of the BOPIM core scaffold is straightforward. A multicomponent one-pot reaction with 4-ethynyl-benzaldehyde and 2-cyanopyridine as starting materials gives target ligand **L** in high yield (75%). By treating the ligand with BF₃·OEt₂ under basic conditions, the intermediate **BOPIM-S** was obtained as a yellow powder with 35% yield after purification by column chromatography. It is well known that non-conjugated alkyne groups can undergo

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Scheme 1. Synthetic route of BOPIM derivatives.

copper catalysed azide–alkyne-cycloaddition (CuAAC) reaction with aliphatic azides efficiently under mild reaction conditions. However, alkyne moieties conjugated with aromatic rings can also react with aliphatic azides, and even aromatic azides to produce triazole derivatives with high yield, which has been adopted to synthesize highly conjugated polymers.⁶ Three aromatic azides with different electronic environments were synthesized according to previously reported procedure.⁷ By reaction with **BOPIM-S** in a mixture of water/*t*-butanol at 60° under N₂ atmosphere, target conjugated structures were obtained with high yield (over 80%) after purification by column chromatography.

In order to elucidate the packing mode of BOPIM-S in solid state, X-ray single crystal diffraction measurement was performed. As shown in Figure 1, molecules were connected by intermolecular non-covalent bonds to produce a rigid network with limited $\pi - \pi$ interactions. From the side view, the Boron-Fluorine chromophore core is almost in the same plane with 4-substituted phenyl ring, however, 5-phenyl ring is twisted and nearly perpendicular to this plane. This phenyl ring acts as an obstacle to enlarge the distance between two neighbouring molecules. This packing mode makes the chromophore core only partially overlap with the neighbouring 4-phenyl ring, but the distance between the two planes is over 3.30 Å due to the existence of twisted 5-phenyl ring. And the intermolecular contacts C6...C11 (3.39 Å) and C7...C10 (3.31 Å) further rigidifies this structure. From the top view, all the molecules are lined almost planar. Interestingly, the chromophore core interacts with neighbouring alkyne groups to produce a tetragonal structure by contacts B1...H16 (3.04 Å), F2...H16 (2.49 Å) and N2...H24 (2.38 Å). In this packing mode, the closed distance of the intermolecular aromatic rings was found to be 13.88 Å.

Physical properties of **BOPIM-S** were measured in solution, and also solid film. All BOPIM dyes reported previously show solventdependent absorption and fluorescence, and it is also the case for **BOPIM-S**. In chloroform its maximum absorption is centred at 414 nm, showing a broad absorption band. With solvent polarity increasing, its absorption blue-shifts to high energy wavelength (Table 1). However, different from other BOPIM dyes, the emissive band of **BOPIM-S** shifts slightly with solvent polarity changing, located around 525 nm. Typical BODIPY dyes show small Stokes shift, which would result in self-absorption of its fluorescence, however, BOPIM dyes usually exhibit large Stokes shift due to the efficient ICT process. The Stokes shifts of BOPIM-S in all the studied solvents are found to be over 100 nm and there is negligible spectral overlap between its absorption and fluorescence (Fig. 2A), which would suppress Forster-type energy transfer and enhance emission intensity. It is worth to note that it shows high fluorescence quantum yield in all studied solvents. The lowest quantum yield is found to be 0.25 in methanol. For a comparison, the BOPIM dye with no alkyne groups emits at 534 nm with quantum yield 0.10 in methanol.^{5a} In chloroform, the value reaches 0.68 for BOPIM-S. Most importantly, intense emission was observed in solid powder and also crystals. And it is exciting that the fluorescent band in amorphous solid film is almost identical with that in dilute THF solution, indicating there is almost no aggregate formation in solid state. To verify this hypothesis, concentrationdependent fluorescent analysis was conducted in chloroform solutions. As shown in Figure 2B, its emission wavelength is independent of concentration, further proving that it can resist aggregate formation in concentrated solution or even solid state. This phenomenon has been observed for other BOPIM dyes, however, its high fluorescence quantum yield is unusual. The terminal groups conjugated to the imidazoles should be a key factor for its high fluorescence quantum yield and aggregate-resistance ability. When terminal groups are halogen atoms or methoxyl moieties which can easily form intermolecular non-covalent bonds, they can make the structure more rigid and less flexible, thus alleviating energy loss through bond rotation. Alkyne is also a well-known group that can form intermolecular non-covalent interactions, which has been proved by X-ray single crystal analysis discussed above. Therefore, it exhibits excellent fluorescent properties both in solution and in solid state.

The terminal groups conjugated to the chromophore core could severely affect the dyes' photophysical properties. Electron-donating groups facilitates intramolecular charge transfer (ICT) process from electron-rich groups to electron-accepting BOPIM skeleton, thus red-shifts the absorption and emission. For the BOPIM dyes synthesized by 'click' chemistry, although the terminal dimethylamino, hydrogen and ester are conjugated to the chromophore

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Figure 1. Crystal packing of BOPIM-S (A) side view; (B) top view.

Table 1

Photophysical data of BOPIM dyes in various solvents

Dyes	solvent	UV		Fluorescence		
		λ_{abs} (nm)	ε (×10 ⁴)	$\lambda_{\rm em}$ (nm)	v (nm)	$arPsi_{ m F}$
BOPIM-S	CHCl ₃	414	1.39	520	106	0.68
	THF	403	1.47	527	124	0.50
	Dioxane	405	0.65	525	120	0.59
	CH ₃ OH	386	1.38	526	140	0.25
	Solid	406	-	526	120	0.31
BOPIM-1	CHCl ₃	427	1.15	537	110	0.39
	THF	415	1.28	544	129	0.22
	Dioxane	417	1.31	543	126	0.24
	CH ₃ OH	391	1.24	531	140	0.01
	Solid	412	-	544	132	0.01
BOPIM-2	CHCl ₃	423	1.40	533	110	0.91
	THF	413	1.35	541	128	0.60
	Dioxane	417	1.18	539	122	0.31
	CH ₃ OH	393	1.35	535	142	0.30
	Solid	412	-	540	128	0.28
BOPIM-3	CHCl ₃	419	1.52	534	115	0.43
	THF	409	1.27	542	133	0.40
	Dioxane	398	1.39	547	149	0.15
	CH ₃ OH	387	1.56	538	151	0.23
	Solid	426	-	531	105	0.26

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Figure 2. (A) Absorption and fluorescent spectra of **BOPIM-S** in solution (THF, 10^{-5} M) and in solid film; (B) concentration-dependent fluorescent spectra in chloroform.

core, they scarcely affect the dyes' absorption and fluorescence. As shown in Figure 3, their absorption and fluorescence are almost in the same pattern in dilute solutions. The maximum absorption band is located around 410 nm in mid-polar solvents, and their fluorescence is around 540 nm. Similar to BOPIM-S, their absorption bands blue-shift with solvent polarity increasing, but their fluorescence bands are almost independent of solvent polarity. Compared to **BOPIM-S**, their absorption and fluorescence shift to longer wavelengths because of the enhanced conjugation degree. However, it seems that the chromophore is mostly affected by triazole ring, and the electron donor (dimethylamino) and acceptor (ester) do not induce obvious differences. This is inconsistent with our previous observations,^{5c} and may be explained by the poor overlap of the π electrons on triazoles and terminal phenyl rings. DFT calculations were performed for these compounds, suggesting that the HOMO distributions primarily reside on the atomic orbitals from triazole to Boron-Fluorine centre, while LUMO was mainly contributed by BOPIM chromophore (Fig. S1). Therefore, the terminal aromatic phenyl rings with functional groups do not severely affect their photophysical properties. The fluorescence quantum yield of **BOPIM-1** is found to be the lowest among the three, which should be due to energy loss via fast rotation of dimethylamino groups. BOPIM-2 and BOPIM-3 exhibit intense emission in solid state (Fig. 3D), mainly due to that aggregate formation is inhibited due to their non-parallel packing mode. But they show slight fluorescence difference in solid state, which may be aroused by the steric effect and supramolecular interac-



Figure 3. (A) Absorption and (B) fluorescent spectra of synthesized BOPIM dyes in solution (THF, 10^{-5} M); (C) absorption and (D) fluorescent spectra of synthesized BOPIM dyes in solid film.

tions of the terminal moieties. And their Stokes shifts are all over 110 nm in solution and also in solid state.

In conclusion, we designed and synthesized a highly solidemissive BOPIM scaffold core with conjugated alkyne groups. The synthesized **BOPIM-S** can undergo CuAAC with aromatic azides efficiently to provide conjugated solid-emissive dyes with different functional groups.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet. 2013.05.116.

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