Design, synthesis and optical properties of carbazole-based halogen-bonded organic semiconductors

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SMART PHOTONIC MATERIALS

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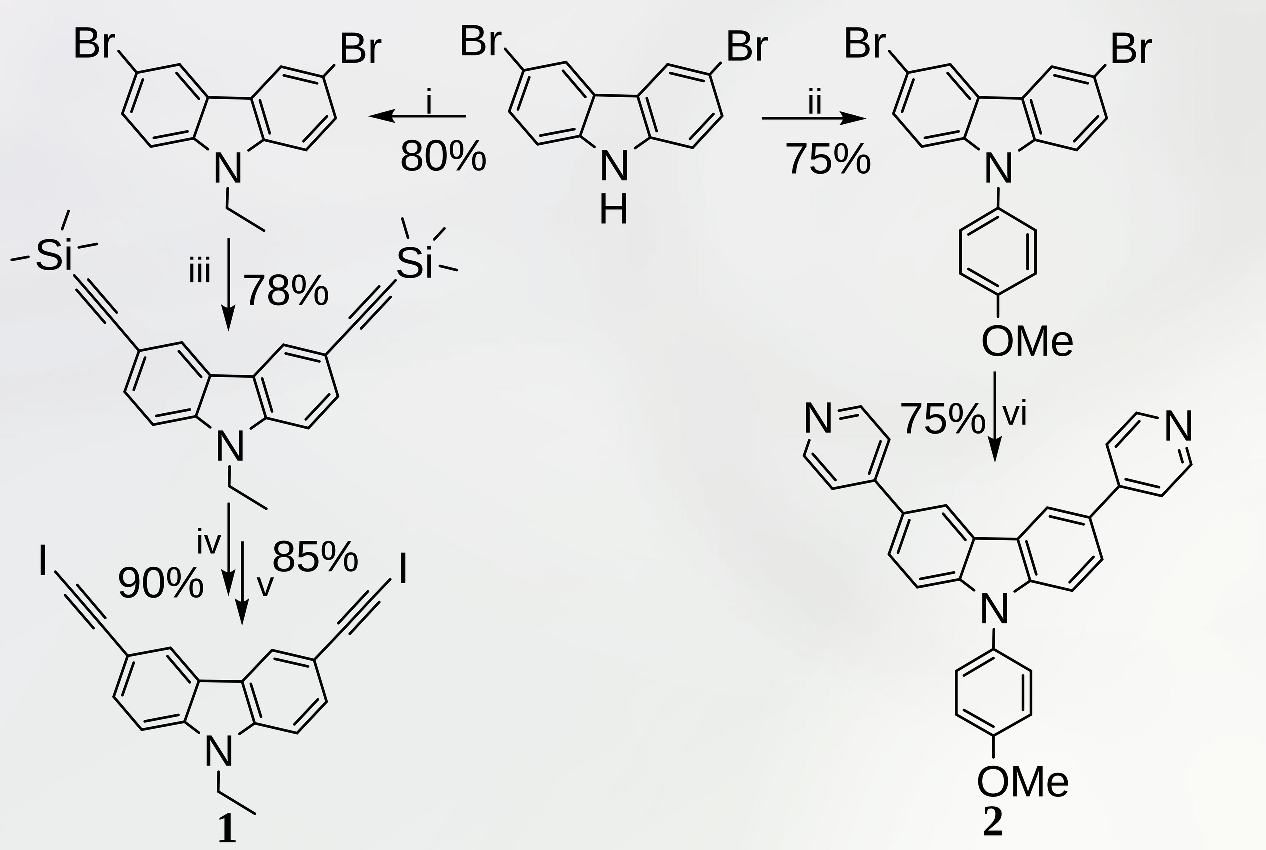
Introduction

Organic-semiconductor-based devices show promise as next-generation electronics platform due to low cost, large-scale manufacturing, and flexibility. Among the critical challenges is the control over molecular packing in organic electronic devices, which dictates properties such as charge-carrier mobility and luminescence efficiency. Offering high purity and well-defined solid-state arrangement, organic crystals are of particular interest for organic electronic devices.[1] Compared to single-component crystals, co-crystals are more versatile since the properties of the final material could be finely tuned by subtle structural variations of the starting modules.[2] Being an effective supramolecular tool in crystal engineering,[3] halogen bonding may offer significant advances in devising novel organic electronic materials. Herein, we present our preliminary results on the design and fabrication of halogen-bonded, carbazole-based luminescent cocrystals.

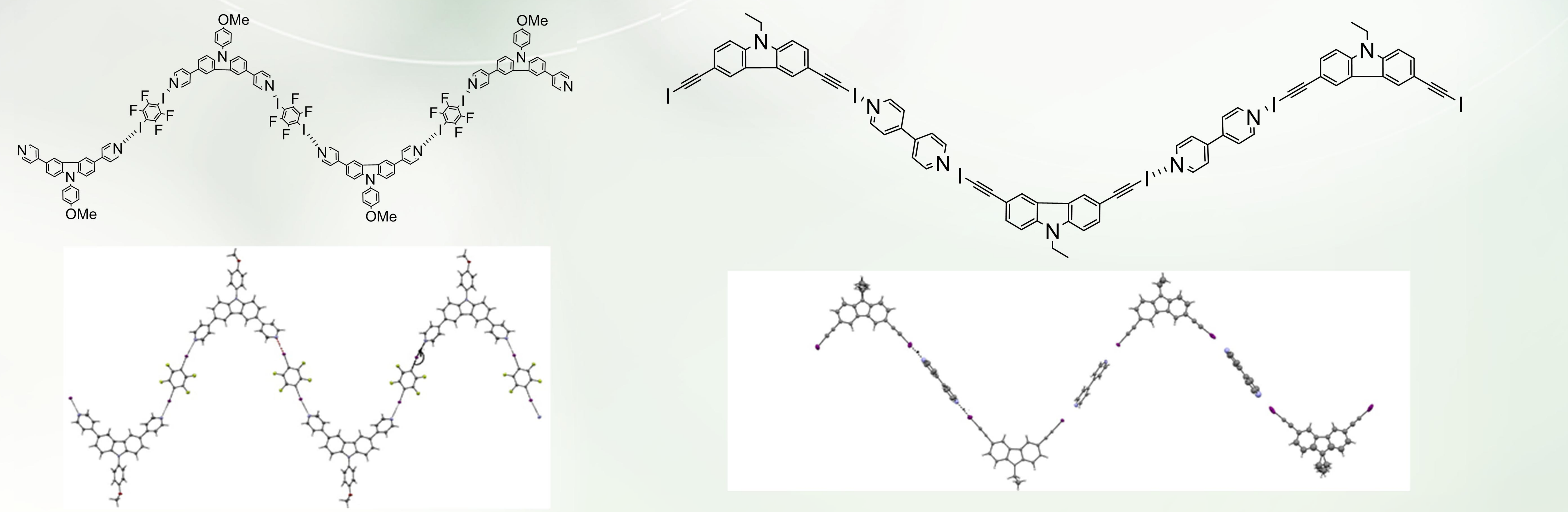
Materials and Methods

Synthetic scheme



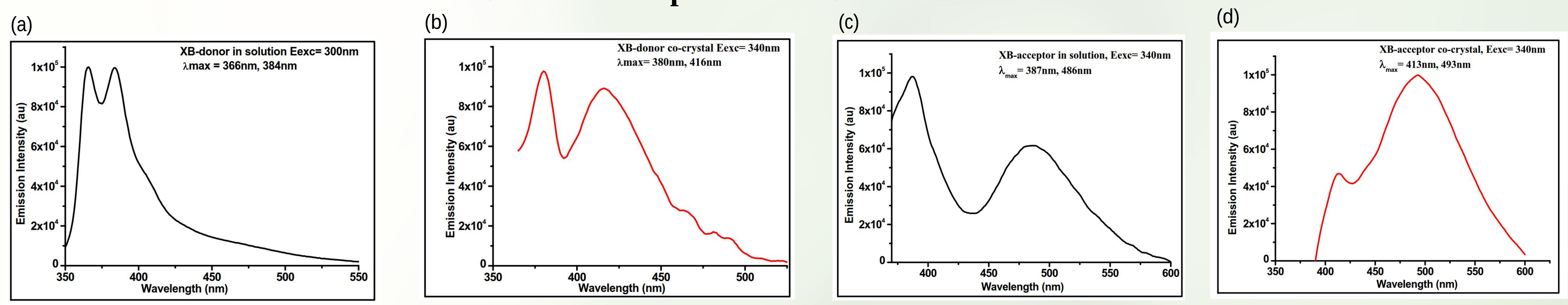
Reagents: i) Ethyl iodide, KOH, DMSO, RT, 12 hr. **ii)** 4-Iodoanisole, K_2CO_3, Cu, DMSO, 120 °C, 24 hr. **iii)** Trimethyl-silylacetylene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, triethylamine, Toluene, 80 °C, 24 hr. **iv)** K_2CO_3, MeOH, 12 hr. **v)** 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), I_2, THF, 6 hr. **vi)** Pyridine-4-boronic acid pinacol ester, $Pd(PPh_3)_4$, THF, 80 °C, 24 hr.

Co-crystallization and crystal structures



The crystal packing of the complexes between **2** and 1-4,diiodotetrafluorobenzene (left) and **1** and 4-4'.bipyridine (right). A short I–N halogen bond is the driving force that leads to the formation of a bidimensional zigzag structure. Ellipsoids are at 50% probability. The I–N halogen bond was also confirmed via infrared spectroscopy.

Photoluminescence spectra in solution and in the solid state



Photoluminescence of the halogen-bond donor **1** in solution (a) and in the solid state (co-crystal with 4,4'-dipyridine) (b). Photoluminescence of the halogen-bond acceptor **2** in solution (c) and in the solid state (co-crystal with 1,4-diiodotetrafluorobenzene) (d). Especially the cocrystal of **1** shows a significant red-shift in λ_{max} compared to the solution spectrum.

Summary

In this work we focus on carbazole-based systems functionalized with XB-donor and acceptor moieties, as shown in the synthetic scheme. Carbazole derivatives have several good qualities such as easy availability, low cost, high solubility, excellent luminescence, and high thermal and chemical stability, making them good candidates especially for OLED applications.[4]

We have obtained halogen-bonded carbazole co-crystals with different light-emitting characteristics. Next we will study in detail the photoluminescence, and in longer term, the electroluminescence properties of our materials, with the aim of controlling the emission properties via crystal engineering. We believe that this design approach can be helpful for the future carbazole-based OLED devices.

References:

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