Fluorescent trifluoromethylated imidazo[1,5-a]pyridines and their application in luminescent down-shifting conversion

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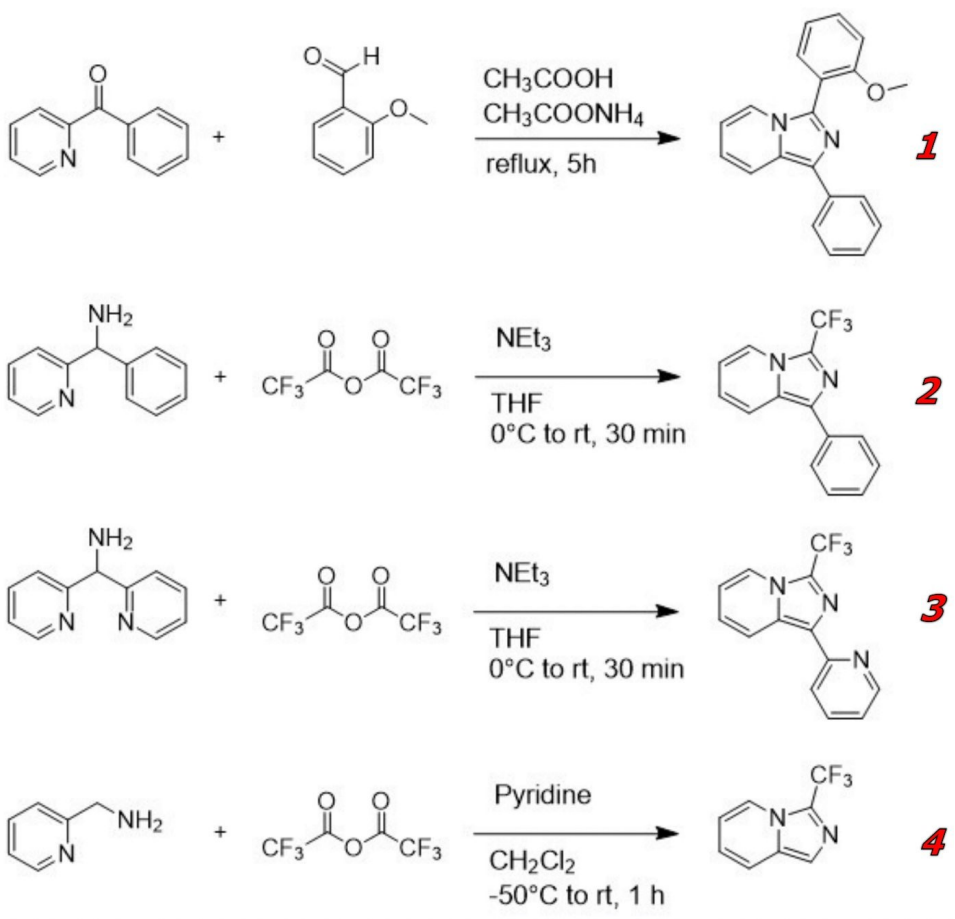
INTRODUCTION

- The increasing demand for efficient, stable and low-cost down-shifting materials is pushing for new practical and tuneable fluorophores based on non-critical raw materials. Recently, small luminescent organic molecules are attracting much interest due to their high stability, structural flexibility and optical tunability.
- Imidazo[1,5-a]pyridine nucleus represents an excellent candidate as emissive heterocycle, thanks to the low cost and its distinctive large Stokes shift.
- A series of imidazo[1,5-a]pyridines with trifluoromethyl group in position 3 and different modifications (phenyl, pyridine or hydrogen) in position 1 has been synthesized and optically characterized both in solution and in host-guest polyurethane matrix.
- As a proof of concept, down-shifting PU coatings have been finally tested on Si-based solar cell to improve the photovoltaic performance.

SYNTHETIC PROCEDURES

- **Compounds 1–4** are based on the fluorescent **imidazo[1,5-a]pyridine** nucleus, obtained by different synthetic approaches.
- The **cyclization reaction** is tolerant to various substrates and, generally, it consists of a **single reaction step** and does not require any highly sensitive reagent or catalyst, employing **available and cheap precursors**.

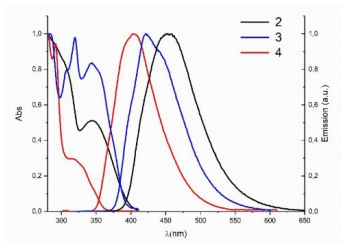


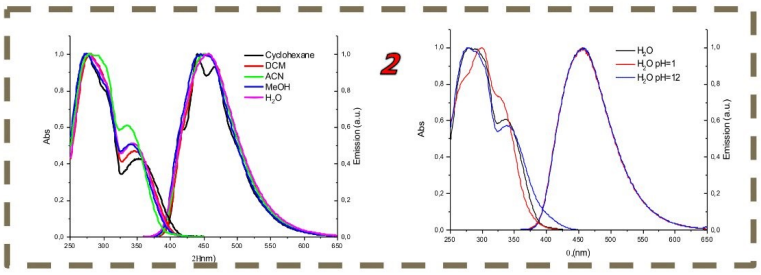
OPTICAL CHARACTERIZATIONS

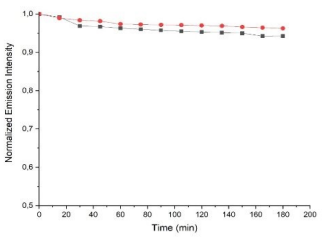
in solution

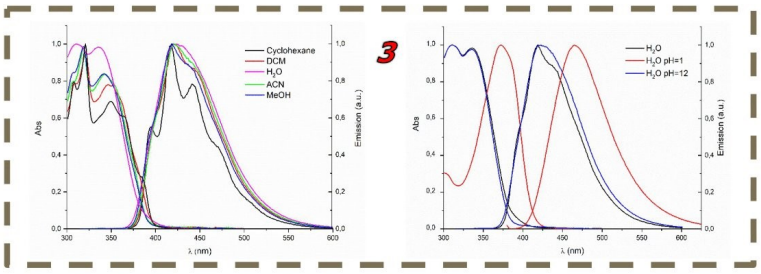
Comp.	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (nm)	log ε ($M^{-1}cm^{-1}$)	Φ (%)
1	301, 374sh	474	178	4.36, 3.86sh	19
2	279, 344	453	109	4.11, 3.81	31
3	283, 320, 343	420	77	4.14, 4.13, 4.06	39
4	281, 292, 317sh	404	112	3.88, 3.85, 3.35sh	13

Suitable optical properties







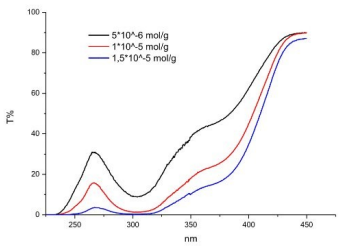


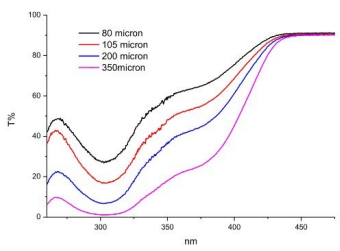
in polyurethane host

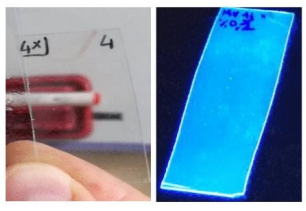
Compounds **1-4** were dissolved in EtOAc, then mixed in polyurethane resin (isocyanate DK180/polyol LCR280RT 3:4, from Special Engines srl) and cast to produce films with defined thickness.

Comp.	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (nm)	log ε ($M^{-1}cm^{-1}$)	Φ (%)
1	302, 374sh	459	157	4.09, 3.59	47
2	280, 345	438	93	4.05, 3.81	58
3	285, 321, 346	420sh, 440	94	4.02, 4.01, 3.94	51
4	281, 291, 323sh	399	108	3.57, 3.53, 3.13sh	10

Increased quantum yield



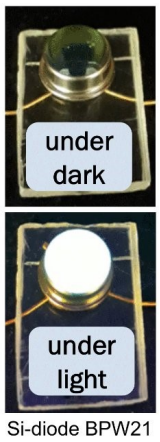




DOWN-SHIFTING COATINGS FOR SOLAR CELLS

Compounds **2** and **3** have been tested in down-shifting PU coatings to increase the photovoltaic performance of commercial silicon solar cells.

Coating (5 mg)	Concentration (10^{-5} mol/g)	I_{sc} (mA)	ΔI_{sc} (mA)	PCE (%)	ΔPCE (%)
Only PU	0	1.16	-	6.42	-
PU + 2	0.5	1.19	+2.6	6.54	+1.9
	1.0	1.17	+0.9	6.50	+1.2
	1.5	1.15	-0.9	6.41	-0.2
PU + 3	0.5	1.20	+3.4	6.59	+2.6
	1.0	1.18	+1.7	6.47	+0.8
	1.5	1.17	+0.9	6.38	-0.6
PU + Lumogen F Violet 570	0.5	1.18	+1.7	6.52	+1.6
	1.0	1.18	+1.7	6.49	+1.1
	1.5	1.16	+0.0	6.43	+0.2



Si-diode BPW21

CONCLUSIONS

✓ The **trifluoromethyl group** in position 3 on the imidazo[1,5-a]pyridine nucleus and the pendant group (**phenyl or pyridine**) in position 1 strongly and positively affect the optical properties, showing **hyperchromic effect and higher quantum yield**. Contrariwise, the elimination of the pendant group has opposite and negative effect.

✓ **Polyurethane films** doped with imidazo[1,5-a]pyridines show good Stokes shift with extraordinary **increase of the quantum yields**, as desired for down-shifting applications.

✓ PU **coatings doped with 2 and 3** increase the photoconversion efficiency of Si-cells, proving imidazo[1,5-a]pyridines are **promising candidates for down-shifting applications**.

References [1] X. Huang, S. Han, W. Huang, X. Liu, *Chem. Soc. Rev.*, (**2013**), *42*, 173–201. **[2]** G. Volpi, R. Rabezzana, *New J. Chem.*, (**2021**), *45* (13). **[3]** G. Volpi, G. Magnano, I. Benesperi, D. Saccone, E. Priola, V. Gianotti, M. Milanesio, E. Conterosito, C. Barolo, G. Viscardi, *Dyes Pigments*, (**2017**), *137*, 152-164. **[4]** G. Volpi, C. Garino, E. Fresta, E. Casamassa, M. Giordano, C. Barolo, G. Viscardi, *Dyes Pigments*, (**2021**), *192*, 109455.

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