

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF NOVEL PYRIMIDINE-BASED DONOR-ACCEPTOR EMITTERS

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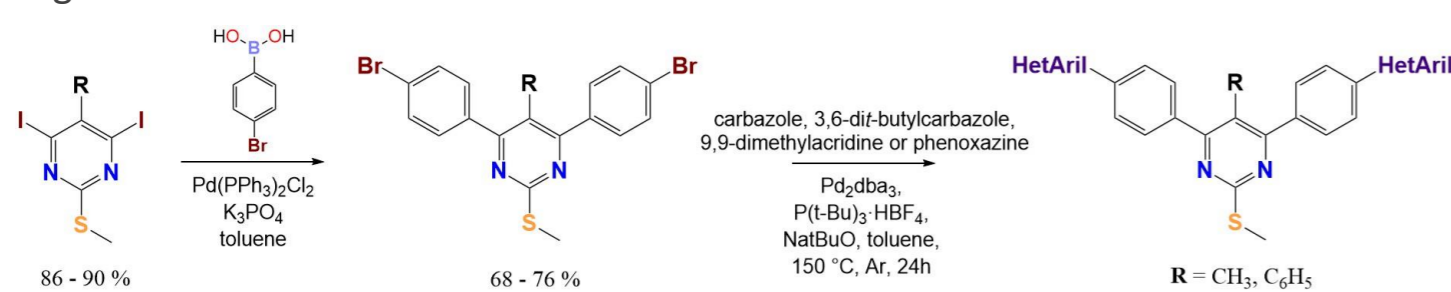
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Introduction

TADF compounds are perfect candidates as the third generation emitters for OLED devices due to low synthesis cost (no noble metals atoms), emission yield reaching near unity [1] and efficient utilization of triplet excitons [2]. Triplet upconversion in TADF compounds is enabled by lowering the singlet-triplet energy gap (ΔE_{ST}) until the thermally activated reverse intersystem crossing becomes evident [3]. Minimization of ΔE_{ST} can be achieved by decoupling HOMO and LUMO in compounds constructed of donor (D) and acceptor (A) aromatic or heteroaromatic units. Recently, compounds containing pyrimidine heterocycle as an A unit have been demonstrated to be promising for TADF applications [3-5]. As a continuation of our work in the field of pyrimidine TADF emitters, we present herein results on the synthesis and photophysical characterization of novel pyrimidine derivatives bearing carbazole, acridane and phenoxazine moieties as D units.

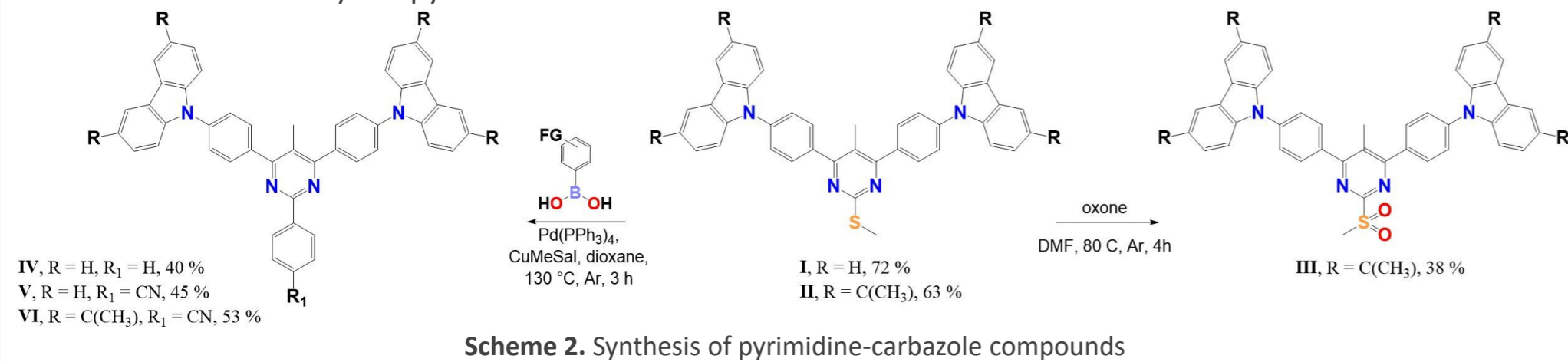
Synthesis

Synthesis of the pyrimidine-based emitters and intermediates was carried out starting from easily accessible 4,6-diiodo-5-methyl(or phenyl)-2-methylthiopyrimidines by a combination of palladium-catalyzed Suzuki-Miyaura and Buchwald-Hartwig amination reactions.



Carbazole derivatives

Seeing the potential of carbazole-pyrimidine pair for achieving efficient deep-blue TADF, we performed the design, synthesis, photophysical characterization as well as application in OLED devices of some novel single bonded carbazole-pyrimidine conjugates. Earlier described synthesis way was expanded by using Liebeskind-Srogl coupling and oxidation of 2-methylthiopyrimidine derivatives.



The photophysical characterization revealed that emission peak tuned in deep-blue region from 400 nm to 433 nm in 1 wt% PMMA polymer matrix. However, most of the compounds had a large separation of lowest singlet and lowest triplet energy levels (ΔE_{ST}) (>500 meV for compounds IV – VI) which led to disabled TADF emission. On the other hand, fast intersystem crossing together with low triplet non-radiative decay allowed for the room temperature phosphorescence (RTP) to be observed. The modification of pyrimidine acceptor unit with stronger moieties containing sulfur atom showed to be superior strategy for TADF emission compared phenyl group. The emission was redshifted without effecting lowest triplet energy level, resulting in lowered ΔE_{ST} . The addition of cyano group to phenyl moiety had a negative effect – the singlet-triplet energy gap was enlarged. The strengthening of donor unit with *t*-butyl groups managed to lower ΔE_{ST} enough (from 480 meV to 310 meV in compounds I and II, respectively and from 687 meV to 501 meV in compounds V and VI, respectively) to observe a weak TADF emission, moreover the quantum yield was increased from 0.32 – 0.43 to around 0.7 for compounds containing *t*-butyl moiety (chart 1).

	Abs _{MAX} , nm	PL _{MAX Tol} , nm	PL _{MAX PMMA} , nm	QY _{air TOL} , nm	QY _{air PMMA} , nm	QY _{vac PMMA} , nm	DF/PF PMMA	ΔE_{ST} , meV	
I	341	406	405	0.18	0.26	0.32		480	RTP
II	348	422	416	0.54	0.64	0.7	0.06	310	TADF+RTP
III	364	446	433	0.59	0.62	0.71	0.25	327	TADF
IV	341	401	400	0.38	0.39	0.41	0.17	500	RTP
V	340	412	407	0.61	0.40	0.43	0.1	687	RTP
VI	348	428	419	0.75	0.66	0.72	0.03	501	TADF+RTP

Chart 1. Photophysical properties of pyrimidine-carbazole derivatives

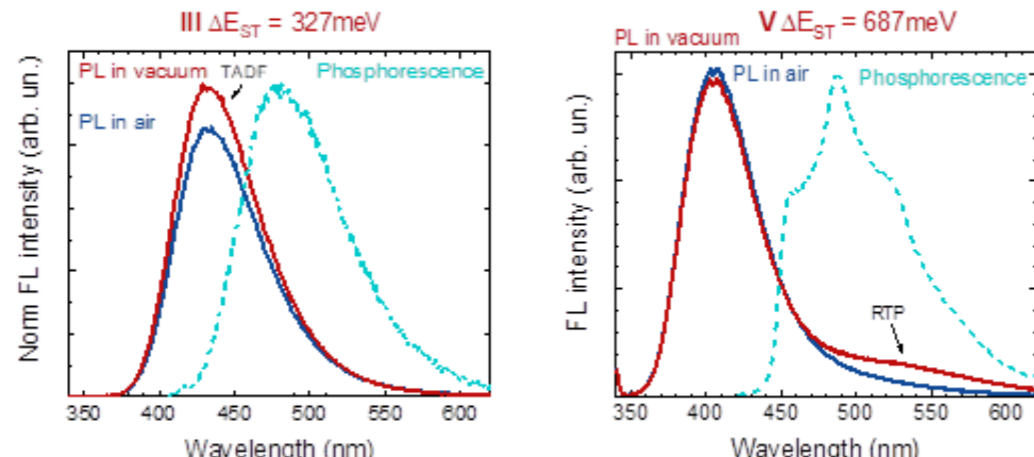
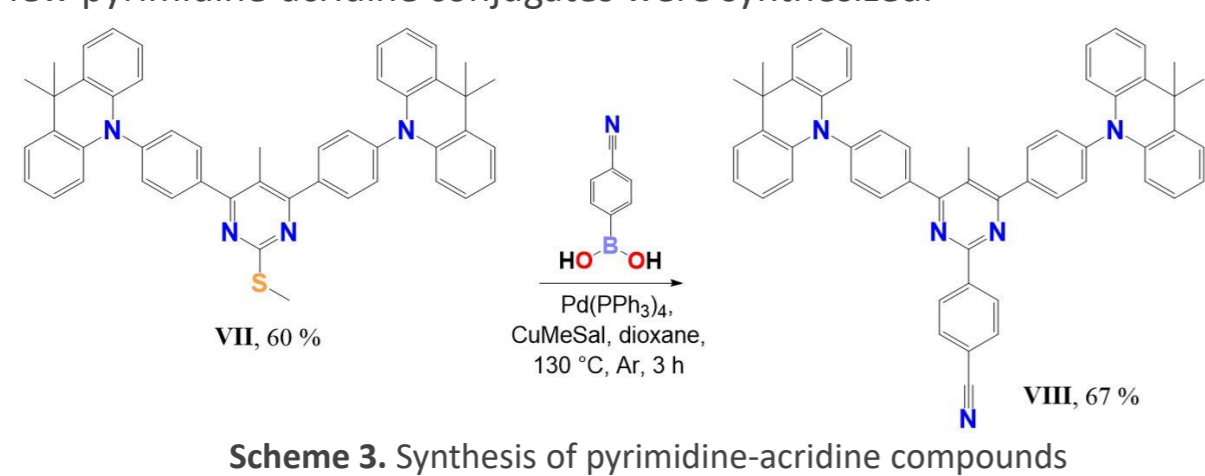


Fig. 1. Graphical representation of some photophysical properties of compounds III and V

Acridine derivatives

Inspired by worldwide trends conditioned by deep-blue fluorescence, as the most required OLED property, of acridine derivatives a few pyrimidine-acridine conjugates were synthesized.



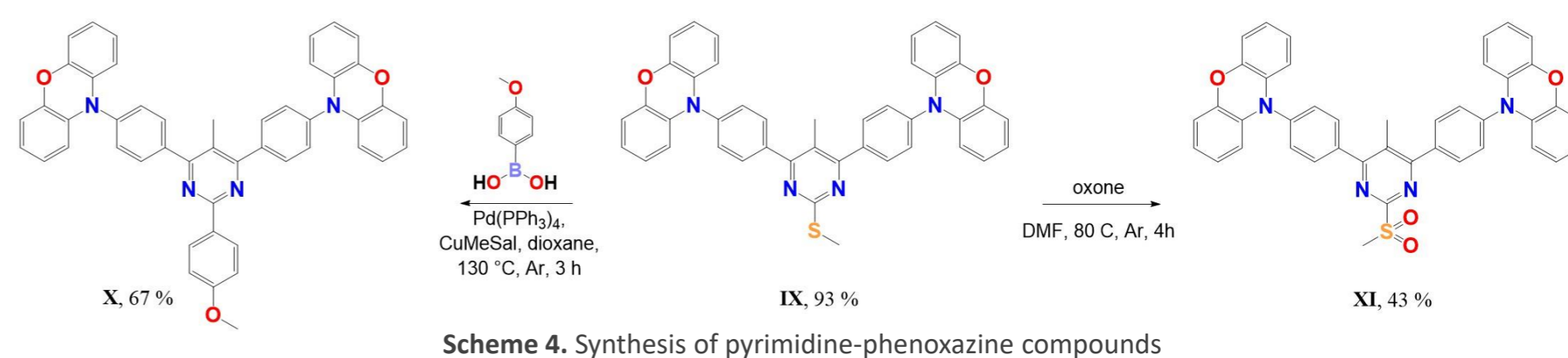
The emission peak was redshifted to ~460 nm by replacing carbazole donor units with 9,9-dimethylacridine moiety. The same acceptor modification strategy was showed to be working in these compounds. The sulfur containing group attached to acceptor unit (VII) showed a reduced ΔE_{ST} (282 meV) compared to 4-cyanophenyl moiety containing compound VIII (334 meV) (chart 2).

	Abs _{MAX} , nm	PL _{MAX Tol} , nm	PL _{MAX PMMA} , nm	QY _{air TOL} , nm	QY _{air PMMA} , nm	QY _{vac PMMA} , nm	DF/PF PMMA	ΔE_{ST} , meV
VII	263	478	461	0.2	0.534	0.708	1.336	282
VIII	283	483	460	0.21	0.44	0.626	1.37	334

Chart 2. Photophysical properties of pyrimidine-acridine derivatives

Phenoxazine derivatives

Greenish thermally activated delayed fluorescence was developed in a material based on a phenoxazine. Compounds were synthesized in the same way as carbazole derivatives discussed above.



Compounds with phenoxazine donor units had their emission shifted to range 488 – 533 nm producing sky-blue – green emission. Here, again, the sulfur containing modification proved to be an efficient ΔE_{ST} lowering strategy. While methoxy-phenyl modification showed extremely large DF/PF ratio of 18.2, it was achieved due to slow decay rate, this, however, led to large roll-off and reduced emission quantum yield. While SO₂ group containing compound XI showed a negligible singlet-triplet energy gap of 6 meV and fastest fluorescence and delayed emission decay rates it suffered from increased non-radiative decay which in turn lowered quantum yield. The largest quantum yield of 0.55 was achieved for compound with SMe modification and ΔE_{ST} = 100 meV (chart 3 and fig. 2).

	Abs _{MAX} , nm	PL _{MAX Tol} , nm	PL _{MAX PMMA} , nm	QY _{air TOL} , nm	QY _{air PMMA} , nm	QY _{vac PMMA} , nm	DF/PF PMMA	ΔE_{ST} , meV
IX	326	531	499	0.185	0.354	0.553	4.87	100
X	327	515	488	0.18	0.15	0.312	18.2	190
XI	405	592	533	0.1	0.36	0.43	1.5	6

Chart 3. Photophysical properties of pyrimidine-phenoxazine derivatives

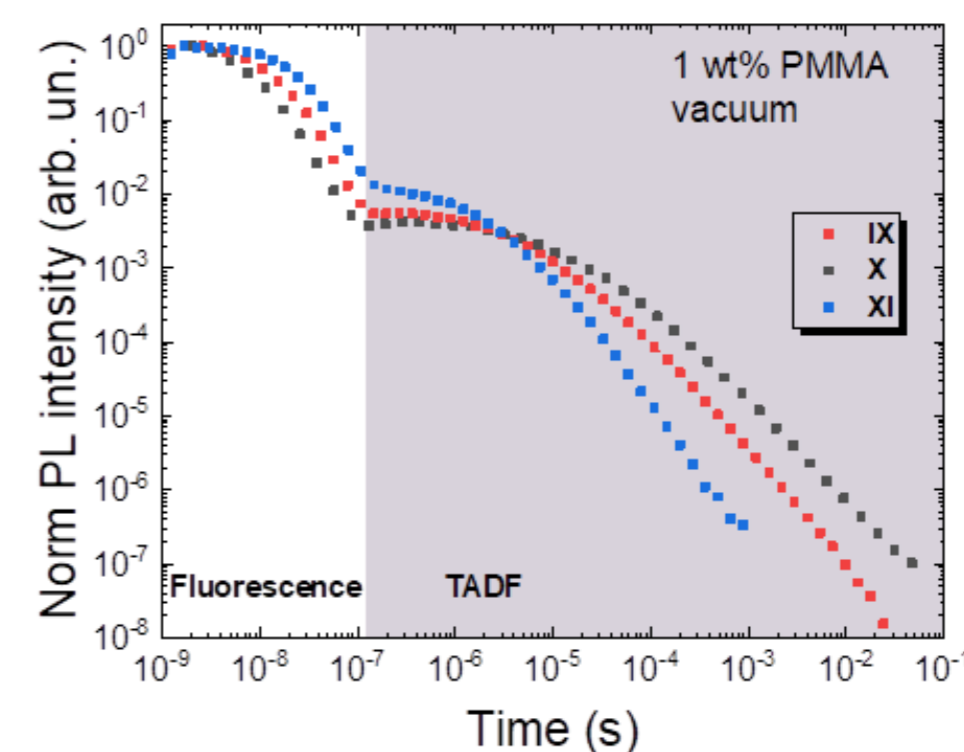
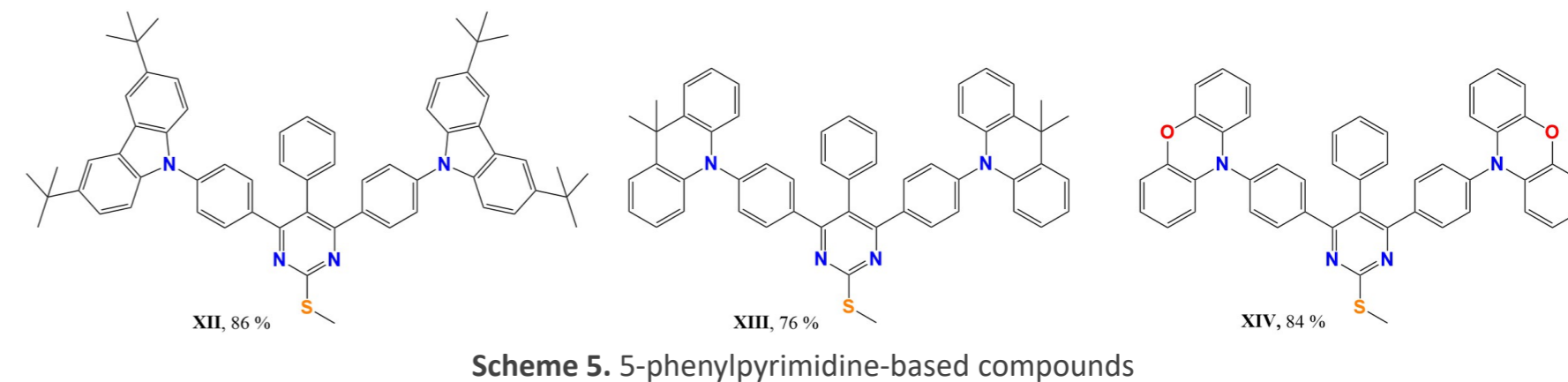


Fig. 2. Decay transients of compounds IX-X in 1 wt% PMMA in vacuum.

5-phenylpyrimidine derivatives

5-phenylpyrimidines should be discussed independently because of their worsening of TADF properties.



In all investigated compounds with various donor units, the introduction of phenyl ring in 5th position led to a small redshift (~10 nm) of emission spectra and decrease in emission quantum yield. Therefore this modification is not suitable for enhancing TADF emitter properties (chart 4).

	Abs _{MAX} , nm	PL _{MAX Tol} , nm	PL _{MAX PMMA} , nm	QY _{air TOL} , nm	QY _{air PMMA} , nm	QY _{vac PMMA} , nm	DF/PF PMMA
XII	364	427	420	0.47	0.1	0.1	0
XIII	346	491	464	0.2	0.11	0.273	16
XIV	391	548	512	0.135	0.274	0.352	2.4

Chart 4. Photophysical properties of 5-phenylpyrimidines

Conclusions

- Starting from an easily accessible 4,6-diiodopyrimidines a general method for the synthesis of novel pyrimidine-based fluorophores has been developed.
- Modification of pyrimidine acceptor with sulfur containing moieties showed to be a successful strategy to reduce singlet-triplet energy gap and increase delayed emission decay rate which was showed to work in compounds with carbazole, 3,6-di-*t*-butylcarbazole, 9,9-dimethylacridine and phenoxazine donor groups.
- The strengthen of carbazole donor units with *t*-butyl groups at 3rd and 6th positions leads to reduced ΔE_{ST} energy bandgap enabling TADF emission and increased quantum yield.
- The modifications of pyrimidine-based TADF emitters showed multiple ways to enhance delayed emission yield laying groundwork for further work developing efficient OLED devices.

Acknowledgements

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