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Unprecedented Binary Cu(I)/Cu(II) Catalyzed One-Pot, Three-Component Synthesis and Evaluation of Luminescent Property of 2-Amino-3-iminoethenylidene-2-indolones: A New Class of Merocyanine Dye Analogues

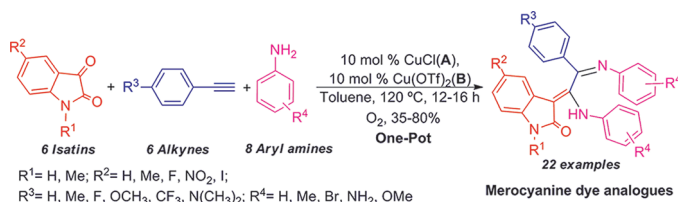
Somasundharam Periyaraja,[†] Asit Baran Mandal,[‡] and Ponnusamy Shanmugam^{*,†}

Council of Scientific and Industrial Research (CSIR)-Central Leather Research Institute (CLRI), Organic Chemistry Division, Chemical Laboratory, Adyar, Chennai-600020, India

shanmu196@rediffmail.com

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ABSTRACT



A facile and efficient binary Cu(I)/Cu(II) catalyzed one-pot, three-component synthesis of 2-amino-3-iminoethenylidene-2-indolones in excellent yield has been achieved. Remarkably, these newly synthesized, stable merocyanine dye analogues showed strong luminescence in the blue region with large Stokes shifts.

The development of novel multicomponent reactions^{1,2} (MCRs) and domino reactions^{3,4} are of interest for chemists because of high atom economy, their convergent character, synthesis of complex molecules, and simple procedures. For the diversity oriented synthesis of complex molecules, it is desirable to convert readily available materials to the target

compounds via multibond formation in a simple operation.⁵ However, with respect to functional π -electron systems such as those used as chromophores, fluorophores, and electrophores in modern electronics,⁶ photonics,⁷ and biophysical analysis,⁸ this approach is still quite novel.^{9,10} MCRs under transition metal catalysis¹¹ such as the Ag/Cu-catalyzed synthesis of quinolines and indoles have paved the way to manifold classes of heterocycles.¹² A Cu(I)/Cu(II) binary catalytic system was effectively used for the synthesis of nitrogen and oxygen heterocycles by a three-component coupling reaction of an aldehyde, alkyne, and amines.¹³

[†] Organic Chemistry Division.

[‡] Chemical Laboratory.

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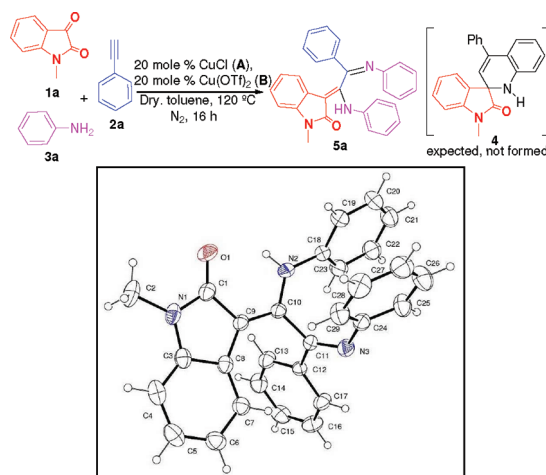
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Merocyanines,¹⁴ i.e. α -donor- ω -acceptor substituted polyenes, have provoked new interest in science and technology,¹⁵ due to their tunable electronic distribution. In addition, merocyanines are also promising chromophores for molecule-based nonlinear optical materials and photovoltaics.¹⁶ General access to these push–pull chromophores has been provided by Knoevenagel condensation¹⁷ or substitution reactions.¹⁸ The synthetic potential of isatin and its derivatives has led to the comprehensive use of this compound in synthetic organic chemistry.¹⁹ We have been working on the novel synthetic applications of isatin derivatives²⁰ for the stereoselective

construction of 3-spiro-2-oxindole derivatives besides several other groups.^{20a–c} Recently, different approaches for the synthesis of merocyanine analogues²¹ have been reported; nevertheless, the starting materials need to be synthesized in a multistep sequence.²² Generally, three-component coupling of an aldehyde, alkyne, and aniline/amine in the presence of Cu(I), known as A³ coupling,²³ is a convenient approach to propargylamines.²⁴ To the best of our knowledge, there has been no report on the application of isatin in the A³ type coupling. However, in our recent work to use isatin in this reaction, we were surprised to find that the reactivity pattern was completely altered. Thus, herein we report a facile and efficient one-pot, three-component binary Cu(I)/Cu(II) catalyzed synthesis of a number of highly stable 2-amino-3-iminoethenylidene-2-indolones, a new class of merocyanine dyes in good yield. Remarkably, the synthesized dyes have showed significant luminescence in the blue region²⁵ with large Stokes shifts.^{20a,b}

Scheme 1. Three Component, One-Pot Synthesis of 2-Amino-3-iminoethenylidene-2-indolone and ORTEP of Compound **5a**



We first found that when a mixture of *N*-methyl isatin **1a**, 1 equiv of phenylacetylene **2a**, 1 equiv of aniline **3a**, 20 mol % CuCl (**A**), and 20 mol % Cu(OTf)₂ (**B**) in toluene was stirred under a nitrogen atmosphere at 120 °C for 16 h, the reaction afforded 2-amino-3-iminoethenylidene-2-indolone **5a** in 20% yield instead of the expected 3-spiroperidine-2-indolone derivative **4**²⁶ (Scheme 1). The structure of **5a** was assigned based on spectroscopic and analytical data (UV–vis, FTIR, ¹H NMR, ¹³C NMR, DEPT-135,

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and FAB-Mass) and unambiguously confirmed by a single crystal X-ray analysis.²⁷

The UV-vis spectrum of compound **5a** showed absorptions at λ_{max} 275 and 352 nm and displayed blue emission at 438 nm by excitation at 352 nm (Figure 1). Thus, compound **5a** is regarded as a new class of merocyanine dye and prompted us to further investigate the reaction condition optimization, scope, mechanism, and the emission characteristics of the products.

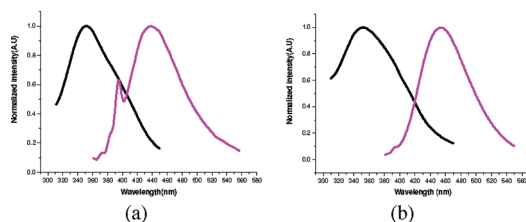
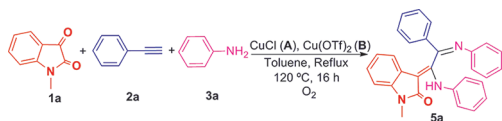


Figure 1. Normalized absorption (black) and emission spectra (magenta) of compounds **5a** (a) and **5i** (b).

To optimize the synthesis of **5a**, a number of experiments with varied mole equivalent reagents, catalysts, and order of addition of reactants have been carried out (Table 1). In a reaction with a mole ratio of reactants **1a:2a:3a** (1:1.5:2) and 20 mol % of each of CuCl and Cu(OTf)₂ catalysts, compound **5a** was isolated in 52% yield (Table 1, entry 3).

Table 1. Reaction Condition Optimization for the Synthesis of 2-Amino-3-iminoethenylidene-2-indolone **5a**



entry	ratio of 1a:2a:3a (equiv)	order of addition of 1a,2a,3a	mole ratio of catalyst (A:B)	yield of 5a (%)
1	1:1:1	1,2,3	20:20	20
2	1:1:1	1,3,2	20:20	trace
3	1:1.5:2	1,2,3	20:20	52
4	1:1.2:2	1,2,3	20:20	58
5	1:1.2:2	1,2,3	05:05	35
6	1:1.2:2	1,2,3	10:10	72^a
7	1:1.2:2	1,2,3	10:00	trace
8	1:1.2:2	1,2,3	00:10	5

^a Reaction was performed under O₂ atmosphere.

Changing the order of addition of reactants did not yield **5a** (Table 1, entry 2), providing information on the intermediate in the reaction. Changing the reactant ratio to 1:1.2:2 and using 10 mol % of each CuCl/Cu(OTf)₂ cooperative catalyst

(27) CCDC 806107 contains the supplementary crystallographic data. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

under an oxygen atmosphere provided **5a** in improved yield (72%), and this was found to be the optimized conditions (Table 1, entry 6). Increasing the moles of alkyne (1.5 equiv) and aniline (2.5 equiv) lead to a complex mixture. The presence of both CuCl and Cu(OTf)₂ catalysts is important since the absence of one of the catalysts resulted in the formation of desired compound **5a** only in a trace amount (Table 1, entries 7 and 8). Lowering the temperature (80 °C) or shortening the time (8 h) resulted in a low yield of **5a**.

In order to demonstrate the scope and limitation of the reaction, experiments with substituted isatins **1a–g**, anilines **3a–h**, and alkynes **2a–f** under optimized conditions have been carried out (Table 2).

Table 2. Various Isatins **1a–g**, Alkynes **2a–f**, and Amines **3a–h**

	R ¹	R ²	1	R ³	2	R ⁴	3
	Me	H	1a	H	2a	H	3a
	H	H	1b	Me	2b	4-Me	3b
	CO ₂ Et	H	1c	F	2c	4-OMe	3c
	Me	Me	1d	OMe	2d	3-Me	3d
	Me	F	1e	CF ₃	2e	2-Et	3e
	Me	NO ₂	1f	N(Me) ₂	2f	2,5-di-Me	3f
	Me	I	1g			4-Br	3g
						4-NH ₂	3h

All the reactions went smoothly and provided corresponding merocyanine dyes **5a–v** in moderate to good yields (Table 3).

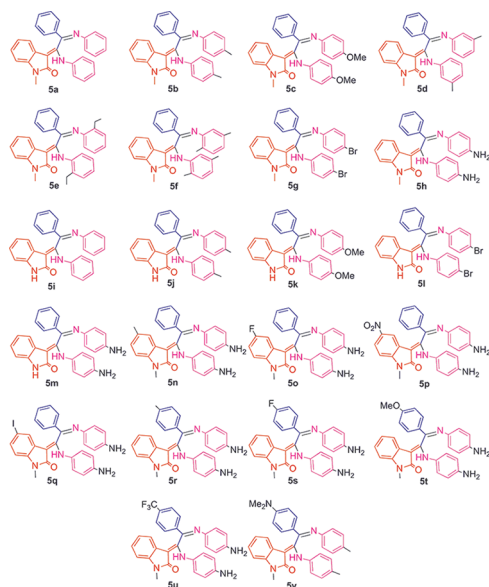
It has been observed that anilines with an electron-releasing group afforded a better yield than aniline. Anilines with a strong electron-withdrawing group such as 4-nitro aniline did not yield any product. However, 4-bromo aniline afforded a moderate yield of the product. Heterocyclic amines such as 2-amino- and 4-aminopyridine failed to provide the desired product, presumably due to weak nucleophilicity. When 4-phenylenediamine (**3h**) was used, considerably higher yields were obtained (Table 2, entries 8 and 13–21). Reaction with 4-aminophenol resulted in a complex mixture due to the availability of a free phenolic group which triggers competitive reactions via the phenoxide ion. Substitutions at the isatin nitrogen have a great effect on the yields of the product as isatin **1b** gave a higher yield than *N*-methylisatin probably due to the higher electrophilicity of the isatin. However, isatin with a strong electron-withdrawing group on nitrogen such as *N*-ethylformate isatin **1c** failed to provide the desired product.

A tentative mechanism of the reaction is proposed in Scheme 2. Accordingly, initially phenylacetylene **2a** reacts with isatin carbonyl **1a** in the presence of binary Cu(I)/Cu(II) catalysts via nucleophilic addition^{26a,28} to provide propargyl alcohol derivative **A**. Activation of a triple bond and 3°-OH group in **A** with Cu(II) followed by the attack of aniline affords allene intermediate **B**. Copper coordination increases the electrophilicity of allene **B**²⁹ which is directly

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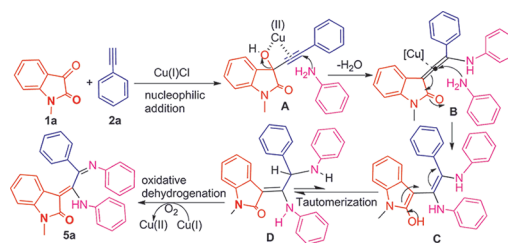
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Table 3. Synthesis of Merocyanine Dyes **5a–v**

entry	isatin	alkyne	amine	product	yield (%)
1	1a	2a	3a	5a	72
2	1a	2a	3b	5b	62
3	1a	2a	3c	5c	65
4	1a	2a	3d	5d	61
5	1a	2a	3e	5e	46
6	1a	2a	3f	5f	58
7	1a	2a	3g	5g	62
8	1a	2a	3h	5h	73
9	1b	2a	3a	5i	72
10	1b	2a	3b	5j	74
11	1b	2a	3c	5k	72
12	1b	2a	3g	5l	70
13	1b	2a	3h	5m	74
14	1d	2a	3h	5n	73
15	1e	2a	3h	5o	75
16	1f	2a	3h	5p	80
17	1g	2a	3h	5q	77
18	1b	2b	3h	5r	70
19	1b	2c	3h	5s	65
20	1b	2d	3h	5t	70
21	1b	2e	3h	5u	75
22	1b	2f	3b	5v	35

attacked by a second molecule of aniline at the allene moiety to give protonated intermediate **C** which tautomerizes to **D**. Under the action of Cu(II), dehydrogenation³⁰ in **D** affords product **5a**. The Cu(I) catalyst is readily oxidized to Cu(II) by oxygen for recyclization.

More interestingly, all the compounds **5a–v** have shown remarkable optical properties (Table 4). Thus, absorption maxima of all the compounds were measured in acetonitrile, and all the compounds showed two major intense absorptions in the ranges 380–350 nm and 275–250 nm (Supporting Information (SI), Table 1). A closer inspection of the solvent polarity effects reveals positive absorption solvatochromism of merocyanine **5a** (SI, Table 2). It should be noted that substitution in aniline causes a significant

Scheme 2. Plausible Mechanism of the Reaction

bathochromic shift in absorption maxima (Table 4, entries 1–6, 350–380 nm). The luminescence of merocyanines **5a**, **h**, **i**, **m**, **s**, **u** in acetonitrile was measured at 298 K (Table 4). The Stokes shifts^{20a,b} $\Delta\nu^{\sim}(\lambda_{\max,\text{abs}} - \lambda_{\max,\text{em}})$ are mostly dependent on the electronic nature of the substituents (R_4). Thus, for the electron-rich 4-phenylenediamine derivative, the Stokes shift is 5421 cm^{-1} and for aniline 6512 cm^{-1} . The above observation indicates that compounds **5a–v** are potential luminescent materials²⁵ for photochemical applications and can be readily synthesized in a one-pot manner.

Table 4. Absorption and Emission Maxima of **5a**, **h**, **i**, **m**, **s**, **u**

entry	product	absorption ^a $\lambda_{\max,\text{abs}}$ (nm)	emission ^{a,b}	
			$\lambda_{\max,\text{em}}$ (nm)	quantum yield $\Phi^{a,c}$
			(Stokes shift, cm^{-1})	
1	5a	275, 352	438 (5578)	0.001
2	5h	254, 377	471 (5294)	0.110
3	5i	254, 351	455 (6512)	0.043
4	5m	254, 379	477 (5421)	0.080
5	5s	257, 374	483 (6034)	0.137
6	5u	259, 383	487 (5576)	0.201

^a Recorded in CH_3CN at 25 °C. ^b Excited at the longest wavelength of the absorption maxima. ^c Determined with quinine sulfate as a standard (0.1 N H_2SO_4) $\Phi_F = 0.54$ at excitation wavelength 366 nm.

In conclusion, we have demonstrated a first one-pot, three-component synthesis of 2-amino-3-iminoethenylidene-2-indolones as a novel class of merocyanine dyes in moderate to good yields. Remarkably, the synthesized dyes have showed luminescence in the blue region and displayed large Stokes shifts in solution. Further work to prepare analogue dyes with better optical properties is currently underway in our laboratory.

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Supporting Information Available. Experimental procedure, tables on solvatochromic effect and absorptions, characterization, and copies of spectra are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.