Solid-state emissive biphenylene bridged bisaroyl-S,N-ketene acetal s as distinct aggregation-induced enhanced emitters and fluorometric probes

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Abstract

Biphenylene bridged bisaroyl-S,N-ketene acetal s can be readily synthesized by a one-pot Masuda borylation-Suzuki arylation sequence, thus, yielding a library of 20 bisaroyl-S,N-ketene acetal s with tunable solid-state emission and aggregation-induced enhanced emission characteristics depending on the para substituent s in the starting material. Potential applications as fluorometric probe of alcoholic beverages are outlined.

KEYWORDS
aggregation-induced emission, aryl-S,N-ketene acetal s, liquor sensors, one-pot reaction, solid-state emission

Since 2019, IUPAC highlights the “Top Ten Emerging Technologies in Chemistry”.[1] This initiative sets out to identify innovations with enormous potential of changing the academic and industrial chemistry as we know it.[2] Last year, aggregation-induced emission (AIE) has been listed as one of these “Top Ten Emerging Technologies in Chemistry”.[2a]

AIE addresses a pressing issue of many luminescent organic materials: in the solid state, the emission of most chromophores is quenched (aggregation-caused quenching, ACQ).[3] Aggregates, however, also offer an elegant solution to this problem[4] and they have received considerable interest in dye chemistry over the past century.[5] A massive boost in academic research was initiated by Tang, who observed the opposite phenomenon of ACQ for 1-methyl-1,2,3,4,5-pentaphenylsilole and therefore coined the term AIE.[4b,6] Typically, AIEgens show barely any luminescence but a strong emission upon aggregation.[3a] The underlying mechanism of AIE is still a hot topic in recent research. Often, this “turn on” of emission upon aggregation is rationalized by restriction of intramolecular motions (RIM)[7] or restricted access to conical intersections (RACI).[8]

The application potential of AIE-active chromophores is enormous[4b,9] and encompasses various research fields like medicinal applications, for instance, in cancer ablation,[10] nanoprobes in tumor-addressing bioimaging,[11] or biosensing and analysis.[12] Additionally, AIEgens have successfully been applied in a plethora of different areas like optoelectronic devices,[13] metal ion detection,[14] data security protection,[15] detection of explosives,[16] or in the generation of white light emission via aggregation-induced dual emission.[17]

While the literature concerning AIE is widely dominated by tetraphenylethene and its derivatives,[18] we could contribute polar heterocyclic systems, such as indolone merocyanines[17,19] and quinoxalines[20], to the field of AIE-related research. Our recent contributions are aryl-S,N-ketene acetal s, low molecular weight merocyanines with tunable solid-state emission, and AIE-behavior, which is strongly dependent on the N-benzyl substituent.[21]

As previously described, the aryl-S,N-ketene acetal s can be accessed via a straightforward base-mediated condensation of acid chlorides 1 and benzoazolium salts 2.[21] The envisioned biphenylene bridged aryl-S,N-ketene acetal s 4 are directly accessible in 30–98% yields from the aryl-S,N-ketene acetal monomers by using the well-established Masuda borylation-Suzuki arylation (MBSA) coupling[22] sequence (Scheme 1). Therefore, an isolation of the intermediary formed borylated aryl-S,N-ketene acetal was not necessary and the bisaroyl-S,N-ketene acetal s were directly obtained starting from the brominated starting material 3. Homo- and hetero bisaroyl-S,N-ketene acetal s alike are accessed by this methodology. Both aryl-S,N-ketene acetal s are mostly connected through the N-benzyl substituent, but as shown, for examples, 4k, 4n, and 4o, a ligation via the aryl moiety can be realized as well. Aroyl-S,N-ketene acetal s can bear electron-donating substituents like dimethylamino,
methoxy, or tert-butyl groups and electron-withdrawing substituents like halides, trifluoromethyl, and cyano groups in para-position as well as heterocyclic aroyl moieties like thiophene (4l, 4s) and furan (4j, 4m, 4p, 4t). It proved beneficial with respect to yields to start the reaction sequence with aroyl-S,N-ketene acetal bearing electron-donating substituents. Generally speaking, furan bearing as well as strongly electron donating substituted and chlorinated aroyl-S,N-ketene acetics gave higher yields than strongly electron withdrawing substituted aroyl-S,N-ketene acetals.

Using the dibrominated aroyl-S,N-ketene acetal 3d, trisaroyl-S,N-ketene acetal 5 can be easily synthesized by employing the same protocol with an increased amount of catalyst, which is necessary to ensure a full conversion of the starting material (Scheme 2).

Bisaroyl-S,N-ketene acetals 4 exhibit two absorption maxima at around 250 and 380–400 nm. Indeed, the absorption spectra match with those of the constituting aroyl-S,N-ketene acetal monomers 3. In contrast to aroyl-S,N-ketene acetal monomers 3, which exhibit, with one exception, no luminescence in organic solvents, the bisaroyl-S,N-ketene acetics 4 emit blue to green light in solution with emission maxima ranging between 470 and 510 nm and Stokes shifts between 3200 and 5800 cm\(^{-1}\). The emission maximum depends on the substituent of the aroyl moiety, the emission maximum is bathochromically shifted with increasing electron donating nature of the substituent. While most bisaroyl-S,N-ketene acetals luminesce rather weakly (fluorescence quantum yields \([\Phi_{em} = 0.01–0.05]\)), dimethylamino substituted bisaroyl-S,N-ketene acetals 4d and e fluoresce more intensively (\([\Phi_{em} = 0.15]\)) as already observed for the respective dimethylamino substituted monomers. Furthermore, after coupling at the aroyl moiety (4k, n, and o), an increase in luminescence intensity is discernable as well (\([\Phi_{em} = 0.09]\)). This can be ascribed to the extended chromophoric system and the formation of a biphenylene bridge, respectively (Figure 1).

For single aroyl-S,N-ketene acetics, a rainbow-colored tuning of solid-state emission by varying the electronic nature of the substituents in para-position of the aroyl moiety is possible. Similarly, the bisaroyl-S,N-ketene acetics 4 are also easily distinguishable by their solid-state emission color ranging from green (4t, \(\lambda_{em} = 503\) nm) to red (4h, \(\lambda_{em} = 633\) nm). Determination of solid-state \(\Phi_{em}\) gave mostly low values for most bisaroyl-S,N-ketene acetals (\([\Phi_{em} = 0.01–0.05]\)), while bisaroyl-S,N-ketene acetals bearing both electron-donating and electron-accepting substituents like 4g possess increased \([\Phi_{em} = \text{values of } 0.13]\) (Figure 1) (for details, see Supporting Information, chpts. 5 and 6).

All aroyl-S,N-ketene acetals show a characteristic AIE behavior, which encouraged us to perform extended AIE studies with bisaroyl-S,N-ketene acetals 4 as well. Bisaroyl-S,N-ketene acetals 4 are easily soluble in most polar organic solvents like acetonitrile, THF, 1,4-dioxane, and alcohols, like ethanol, but insoluble in water. Samples of the bisaroyl-S,N-ketene acetals were dissolved in various solvent/water mixtures. Most distinct results were obtained in ethanol/water mixtures with water contents varying from 0% to 95%, which were consequently used for all AIE studies. The fact that we already observed luminescence in pure ethanol poses bisaroyl-S,N-ketene acetals 4 as AIEE chromophores. Exemplarily, the AIEE behavior of bisaroyl-S,N-ketene acetals will be discussed for dimethylamino-cyano derivative 4e and methoxy-cyano derivative 4g. The AIE characteristics of trimer 5 are summarized in the Supporting Information (chpt. 6).

For bisaroyl-S,N-ketene acetal 4 g, a typical AIEE behavior is observed. At low water fractions up to 40%, nearly no luminescence is detected (\([\Phi_{em} < 0.01]\)). Further increasing the water fraction leads to aggregation of the dye, thus resulting in an enhanced \([\Phi_{em} = 0.09]\). Blocking of nonradiative decay channels of the excited singlet state by aggregation-caused RIM\(^{[7]}\) or RACI\(^{[8]}\) rationalizes the observed AIEE. Raising the water fraction above 80%, the fluorescence intensity decreases due to precipitation of the dye. Alongside the 10-fold increase in fluorescence, the emission maximum is bathochromically shifted from 454 to 500 nm upon aggregation (Figure 2, right). A similar behavior can be observed for trisaroyl-S,N-ketene acetals 4 5 (see Supporting Information, Figure S24.)

For dimethylamino-substituted derivatives 4d and 4e and aroyl-connected bisaroyl-S,N-ketene acetals (4k, n, and o), the fluorescence is quenched upon aggregation, and...
SCHEME 2  One-pot MBSA synthesis of trisaroyl-S,N-ketene acetal 5 (reaction was performed on a 0.25 mmol scale. Reaction yield [in %] is given after flash chromatography on silica gel. For experimental details, see Supporting Information, chpt. 3, p. S60)

![Scheme 2](image_url)

The discernable emission color change of 4f upon aggregation (Figure 3, bottom), which is ascribed to the combination of the strong electron donating methoxy substituted, and the electron donating fluorine substituted arroyl-S,N-ketene acetal unit, which exhibited independently different colors upon aggregation,[21] encouraged us to establish a new naked eye analytics for the determination of the water content of different alcoholic beverages. Organic dyes used as high-end...
analytics for whiskey and other hard liquors by developing assays and chemical tongues have been reported.[23] In comparison, our sensor generates only a rough, yet correct output. Bisaroyl-\(S,N\)-ketene acetal 4f was chosen due to its diverse color spectrum in aggregated form. We analyzed and identified different colorless alcoholic beverages with a specified alcohol content, which resulted in emission spectra of varying intensity and shape (Figure 3). Comparing previous AIEE studies of 4f (Supporting Information, Figure S9) with emission in selected drinks, the water content can be determined although it has to be clarified that it is not possible to distinguish beverages with a water content between 0% and 40% (Figure 3, middle). Only in the case of hazelnut liquor, the optically determined water fraction overestimates the water content of the hazelnut liquor as declared by the manufacturer (Figure 3, middle). The bisaroyl-\(S,N\)-ketene acetal 4f is well suited for the beverage analysis due to its clear emission color distinctness upon aggregation.

In summary, a library of 20 novel biphénylene bridged bisaroyl-\(S,N\)-ketene acetals and one trimer were synthesized in moderate to excellent yields by MBSA sequence starting from arroyl-\(S,N\)-ketene acetal monomers. As known for the monomers, the substitution pattern enables full control of the solid-state emission color and the AIE. In contrast to the monomers, weak blue to green luminescence of bisaroyl-\(S,N\)-ketene acetals in ethanol occurs as well, with
intensities that strongly depend on the connectivity and the substituent pattern. The aggregation-induced change of emission color is well suited for applications in analyte screening as shown by the determination of the water fraction of various alcoholic beverages based on emission color of dissolved dye. Our future work will be directed to develop π-conjugation extended aryl-S,N-ketene acetals as well as bridged aryl-S,N-ketene acetals with tunable AIEE characteristics via one-pot methodologies.

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**CONFLICT OF INTEREST**

We thereby declare that this manuscript has not been published elsewhere and there are no conflicts of interest.

**DATA AVAILABILITY STATEMENT**

The data that support the findings of this study are openly available in the Supporting Information at the end of this document.

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