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Synthesis and optical properties of a library of multi-colored isomeric aryldibenzopyrylium halochromic cations

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ABSTRACT

This report describes the synthesis of five new colorful 6-aryldibenzo[b,d]pyrylium cation salts, a largely unexplored structural unit. These rare compounds are benzannulated structural derivatives of the well-known flavylium cations found widespread in natural pigments. These new dyes are directly compared to three previously synthesized 6-aryldibenzo[b,d]pyrylium cation salts as well as eight colorful isomeric 9-aryldibenzo[b,e]pyrylium cation, or 9-arylxanthylium, salts. The 9-arylxanthylium unit is commonly found in the biologically important rhodamine and rosamine dyes, yet six of the analogs presented in this study were either previously unreported or not isolated. The visual and spectroscopic properties of all 16 compounds were analyzed as a function of the structural differences between the compounds. All compounds displayed reversible halochromism in organic solution, displaying bright colors under acidic conditions and becoming colorless under basic conditions.

1. Introduction

Pyrylium is a well-known aromatic heterocycle containing an oxonium cation (Fig. 1) which forms a wide variety of stable salts with numerous counteranions [1]. Monobenzannulated pyrylium cations, known as chromenylium or isochromenylium, are also common (Fig. 1) [2]. Naturally-occurring pigments known as anthocyanidins, found in blueberries, grapes, roses, cabbage and other colorful vegetation, contain the 2-phenylchromenylium, or flavylium, unit [3]. Isomeric dibenzannulated pyrylium cations, known as dibenzo[b,d]pyrylium or dibenzo[b,e]pyrylium (commonly named xanthylium) are also known. The 9-arylxanthylium unit is commonly found in the ubiquitous biologically relevant rhodamine and rosamine-derived dyes and probes [4–11]. In these cases the xanthylium ion is highly stabilized by strongly electron donating amino substituents at the C3 and C6-positions, causing the amino groups to carry the bulk of the positive charge. Stabilized 9-arylxanthylium containing compounds also continue to find broad application as light harvesting materials for solar cells, photocatalysis, and other related applications [12–18]. Some less stabilized unsubstituted 9-arylxanthyliums have been synthesized and their reactivity and physical properties have been studied [19–25]. In stark contrast to 9-arylxanthyliums, the isomeric 6-aryldibenzo[b,d]pyrylium aromatic heterocycle subunit is comparatively uncommon (Fig. 1). This is rather unexpected since 6-aryldibenzo[b,d]pyrylium salts have the same carbon skeleton as important nitrogen-containing 6-arylphenanthridinium dyes, such as ethidium bromide [26], and are benzannulated analogs of the pervasive flavylium-containing pigments found in nature [3,27].

To expand the library of reported 6-aryldibenzo[b,d]pyrylium salts we had previously reported in a preliminary communication, the synthesis and study of three such colorful salts (**10**–**12** in Scheme 1) [28]. Prior to this report only three 6-aryldibenzo[b,d]pyrylium salts, including **10**, had been prepared in the literature with limited characterization and none reporting halochromism [29–31]. We found that all three compounds **10**–**12** are brightly colored in organic solution and displayed halochromic properties through visual and spectroscopically measurable responses to changes in acidity and basicity in organic solution [28]. The structurally-similar naturally occurring flavylium containing pigments are well known to be sensitive to pH and display halochromism with an optical response; the results of **10**–**12** mirrored those of these known pigments [27]. Nucleophiles have been

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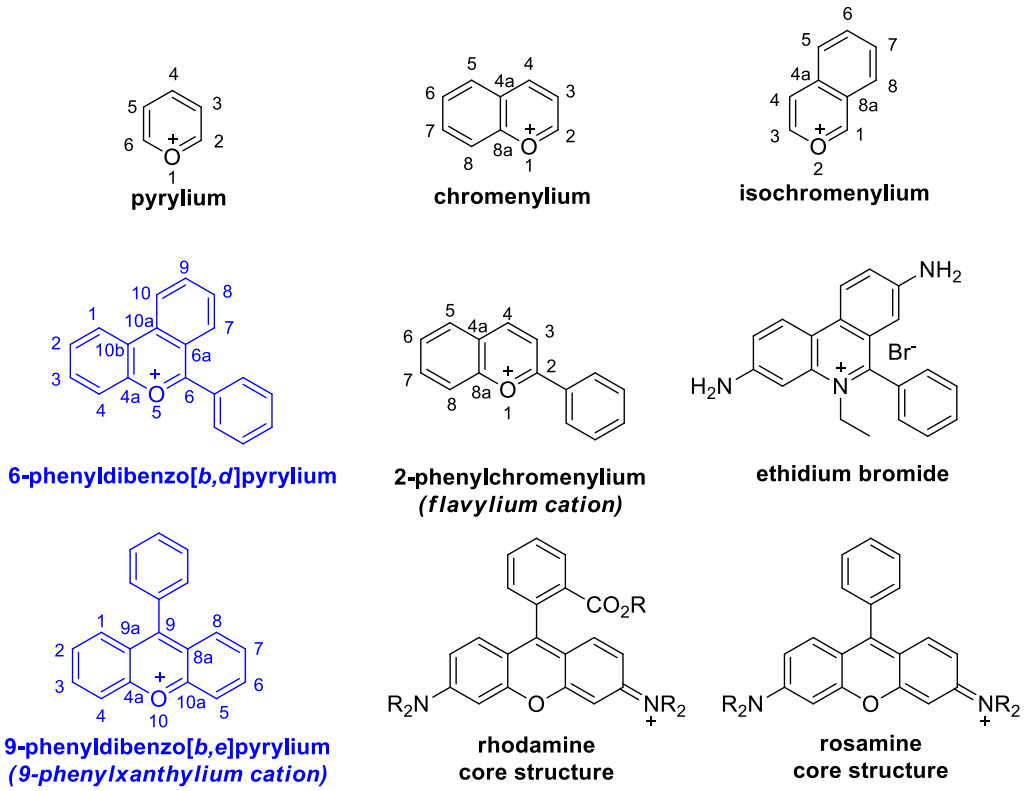

Fig. 1. Structures of different cationic aromatic pyrylium-based heterocycles and their derivates.

shown to attack flavylium cations at the C2 position [27] and are suspected to attack the C6 position [30] of 6-aryldibenzo[*b*,*d*] pyrylium cations, thus disrupting the conjugation in the molecules. This preliminary communication indicated that compounds containing the relatively unexplored 6-aryldibenzo[*b*,*d*]pyrylium subunit are simple to synthesize and could show promise in dye applications and as optical pH sensors [28].

In designing compounds with specific optical properties, it is understood that altering the functional group identity of the donor or altering the conjugation pathway of donor-acceptor compounds has significant effect on the optical properties of donor-acceptor compounds with intramolecular charge transfer (ICT) [32–34]. In this current study, we sought to explore how these alterations in functional groups and conjugation pathways would affect the properties of the still highly unexplored 6-aryldibenzo[b,d]pyrylium cations (Scheme 1) to provide a more extensive picture of the potential of these compounds. To this end we have synthesized five previously unreported colorful 6-aryldibenzo[b,d]pyrylium cations, some isolated in their protonated or semi-protonated forms, containing either shorter monophenyl or longer biphenyl spacer conjugating units containing no donors, weak methoxy donors, or stronger dimethylamino or diphenylamino donors (**13**–**17**). We have found that these structural alterations indeed have significant effect on modulating their optical properties and that all compounds displayed halochromism in organic solution.

With the large variety of 6-aryldibenzo[b,d]pyrylium **10**–**17** cations now in hand for this study (Scheme 1), we sought to compare them to their expectedly more common 9-arylxanthylium analogs **19**–**26** (Scheme 2) to determine what effect, if any, the molecular structure of the dibenzopyrylium unit had on the optical properties of the compounds. However, we discovered that while more complex 9-arylxanthylium based compounds are well researched due to their essential functions in dye and probe applications [4–18], simple analogs with no further substitution at the xanthylium subunit itself are surprisingly rare [19–25]. Of these simpler types of 9-arylxanthylium compounds, only a few have been synthesized, isolated, and studied. This includes unsubstituted **19** and methoxy-containing **20** [19]. Other studies state the in-situ generation of certain 9-arylxanthylium cations but do not report full details on their preparation, nor the isolation or full characterization of the compounds, including dimethylamino-containing **21** [35] and biphenyl-containing **23** [36]. Prior to the study described herein, compounds **22**, **24**–**26** have not been reported in any form and **21** and **23** have been reported *in-situ* but not isolated or characterized fully [35,36]. We were able to synthesize, isolate, and characterize **19**–**26**, some in their protonated or semi-protonated forms, for the purposes of making a direct comparison to their 6-aryldibenzo[b,d]pyrylium **10**–**17** analogs. We have found that, like their 6-aryldibenzo[b,d]pyrylium analogs, the structural alterations in **19**–**26** have significant effect on modulating their optical properties and that all compounds displayed halochromism in organic solution.

2. Results and discussion

2.1. Synthesis

In this current study, 6-aryldibenzo[b,d]pyrylium cations (**10**–**17**) were prepared via addition of the appropriate arylmagnesium bromide (**10**–**12**, **14**, **16**) or aryllithium (**13**, **15**, **17**) to 6H-benzo[*c*]chromen-6-one **9** (Scheme 1). All 9-arylxanthylium cations (**19**–**26**) were prepared similarly via addition of the appropriate arylmagnesium halide (**19, 20**, **23, 24**) or aryllithium (**21**, **22**, **25**) to xanthone **18** (Scheme 2) The intermediate hemiketals **10a**-

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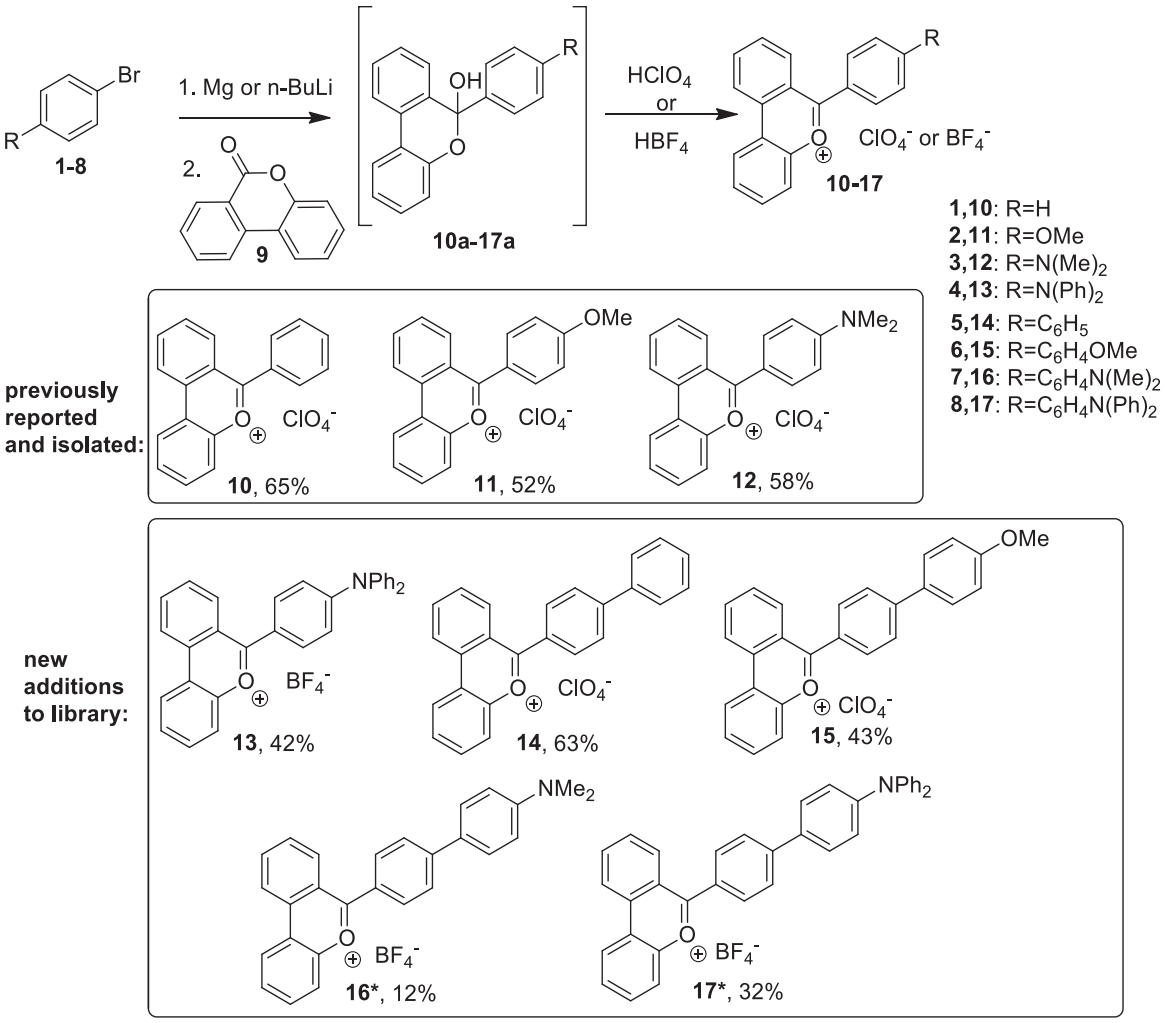

Scheme 1. General Synthesis of Expanded Library of 6-aryldibenzo[b,d]pyrylium salts.

17a or phenylogous hemiketals **19a**-**26a** were directly dehydrated in solutions containing perchloric acid or fluoroboric acid resulting in the desired pyrylium products. Preparation of 6-aryldibenzo[b,d] pyrylium cations **10**–**12** have been described by us previously [28] and their syntheses replicated for this study. 9-arylxanthylium cations **19** [19] and **20** [19] have been previously reported and characterized; their syntheses were repeated for this study. Arylxanthylium **21** [35] has been reported to form via treatment of **21a** with sulfuric acid but had not yet been isolated (Scheme 2) or characterized beyond *in-situ* UV–Vis spectroscopy. Arylxanthylium **22** [36] has also been reported to be generated *in-situ* from its xanthene precursor but was not isolated or characterized. Most of the pyrylium products synthesized were easily precipitated from diethyl ether solutions of their crude alcohol precursors via elimination with aqueous $HClO_4$ (**10**–**12**, **14**, **15**, **19**, **20**, **23**, **24**) or aqueous HBF_4 (**13**, **22**) with or without added acetic anhydride.

Strongly acidic environments are required for conversion of the alcohol precursors (**10a**-**17a**, **19a**-**26a**) into pyrylium structures. Several of these pyrylium products, especially those containing basic amino donor groups further removed from the pyrylium subunit (**16**, **17**, **21**, **25**, **26**), were very sensitive to over-protonation during this elimination step resulting in intractable isolation and characterization. Using an alternative strategy, we found that dimethylamino-containing xanthylium salt **21** could be isolated in its unprotonated forms by careful addition of neat 1:1 tetrafluoroboric acid diethyl ether complex to CH_2Cl_2 solutions containing the purified alcohol precursor **21a**. The solid product was then afforded by carefully layering diethyl ether on top of the solutions and allowing for slow diffusion over several days. Dimethylamino-containing salts **16** and **25**, however, were still found to be too sensitive, regardless of method and careful stoichiometric addition of acid, and could ultimately only be precipitated in their protonated forms, as evidenced by their yellow coloring and corresponding spectral data, discussed below. Analogous diphenylamino-containing salts **17** and **26** were engineered to reduce the acid sensitivity of the amino group, compared to **16** and **25**. However, spectroscopic evidence, discussed below, points to these compounds being isolated in partially protonated forms, regardless of method and careful stoichiometric addition of acid used to form the pyrylium group. Despite this, diphenylamino **17** and **26** are brightly colored blue and green compounds, respectively, in direct contrast to the yellow color of dimethylamino **16** and **25**.

All aryl bromides used in the syntheses of **10**–**17** (Scheme 1) and

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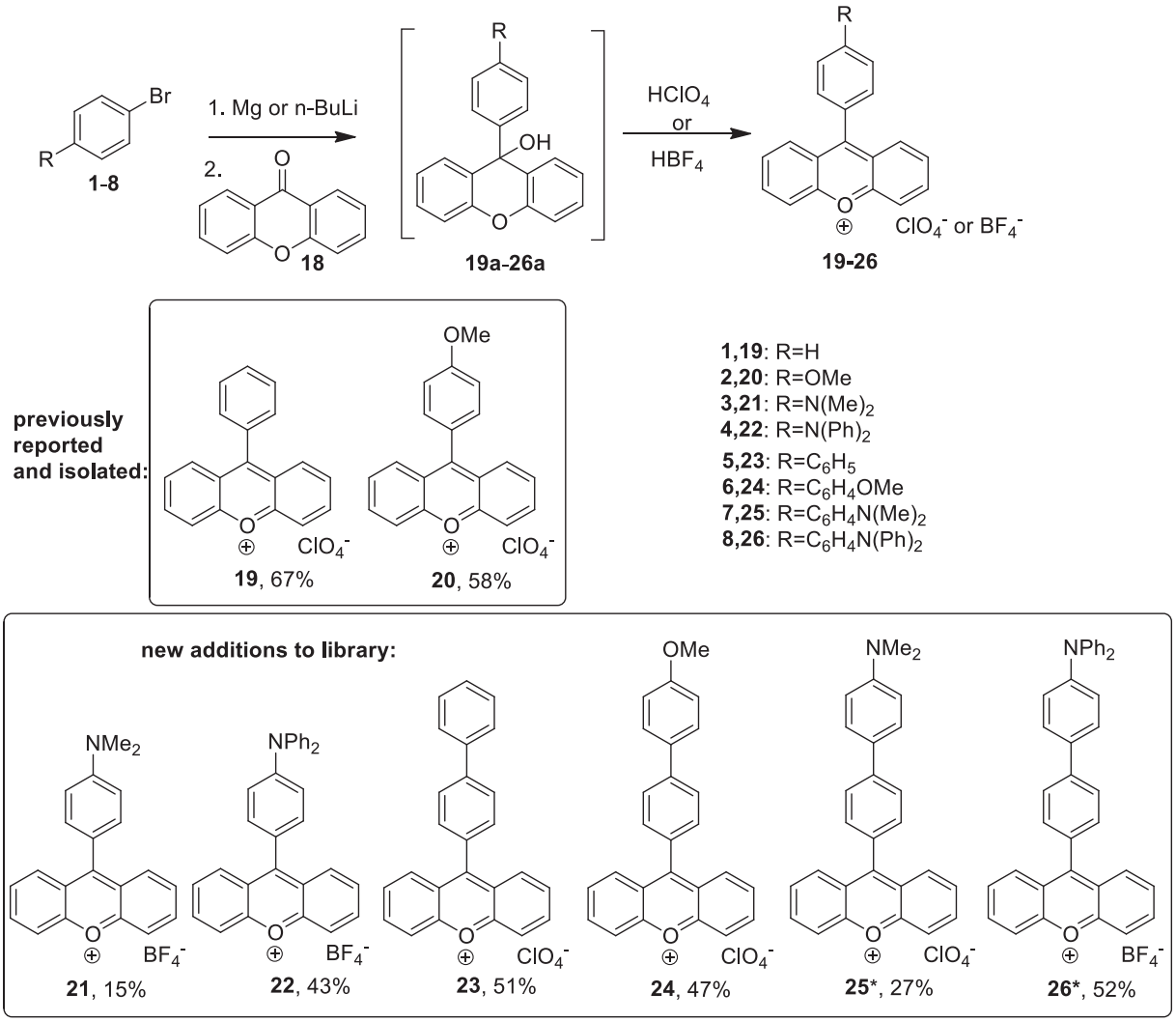

Scheme 2. General Synthesis of Expanded Library of 9-aryldibenzo[b,e]pyrylium (xanthylium) salts.

19–**26** (Scheme 2) are previously known and were either purchased commercially (**1**–**3**, **5**) or prepared via literature methods using Suzuki-Miyaura or Buchwald-Hartwig coupling reactions (**4** [37], **6** [38], **7** [39], **8**, [40]) in acceptable yields. Lactone **9** (Scheme 1) was prepared with a Baeyer-Villiger oxidation of 9-fluorenone as described by us previously [28] and xanthone **18** (Scheme 2) was purchased commercially.

2.2. Visual characterization and comparison

Pyrylium salts **10**–**17** and **19**–**26** display a wide variety of bright and attractive colors in solution (Figs. 2 and 3) upon visual inspection. The salts containing only unsubstituted aryl groups (**10**, **14**, **19**, and **23**) appear yellow or yellow orange. The pyrylium salts that contain donor groups have more vibrant colors. Those containing weaker methoxy donors (**11**, **15**, **20**, and **24**) appear yellow, orange, or red. Those containing stronger amino donors (**12**, **13**, **17**, **21**, **22**, and **26**) display bright purple, blue, and green colors.

The colors visualized from the pyrylium cation solutions are shown to be highly dependent on several factors: (1) the structure of the pyrylium subunit (dibenzo[b,d]pyrylium **10**–**17** or dibenzo [b,e]pyrylium/xanthylium **19**–**26**), the length and structure of the spacer unit connecting the donor to the pyrylium subunit (monophenyl **10**–**13**/**19**–**22** vs biphenyl **14**–**17**/**23**–**26**), and the presence and identity of the donor unit itself (no donor, weaker methoxy donor, or stronger amino donor). The colors displayed by the xanthylium salts are all indicative of a red shift in absorbance relative to the analogous dibenzo[b,d]pyrylium salts. The colors of compounds containing biphenyl spacers are also indicative of a red shift in absorbance relative to the analogous compounds with monophenyl spacers (except for **16** and **25**). Those containing no donor unit are yellow or yellow orange; those with weak donors are yellow, orange, or red; those containing amino donors are purple, blue and green. This demonstrates that colors of pyrylium salts can be directly engineered by simple manipulation of molecular structure resulting in a large array of possible colors.

Visual inspection of **16** and **25** provide evidence of protonation at the amino group due to their yellow coloring compared to the bright blues and purples of **12**, **13**, **21**, and **22**. The protonation of the amino group results in significant attenuation in its ability donate electron density into the oxonium atom of the pyrylium acceptor compared to the other amine containing pyrylium salts. It is known that the degree of pi orbital overlap is reduced due to the extra torsions and therefore unfavorable geometries in oligophenyl

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Fig. 2. Photographs of 6-aryldibenzo[b,d]pyrylium salts **10**–**17** in solution. **Top**: Vials containing 2 mL solutions of **10**–**17**, 1.0 mM in CH_3CN. **Middle**: Vials from the top after addition of 40 μL of TEA. **Bottom**: Vials from the middle after addition of 120 μL of TFA.

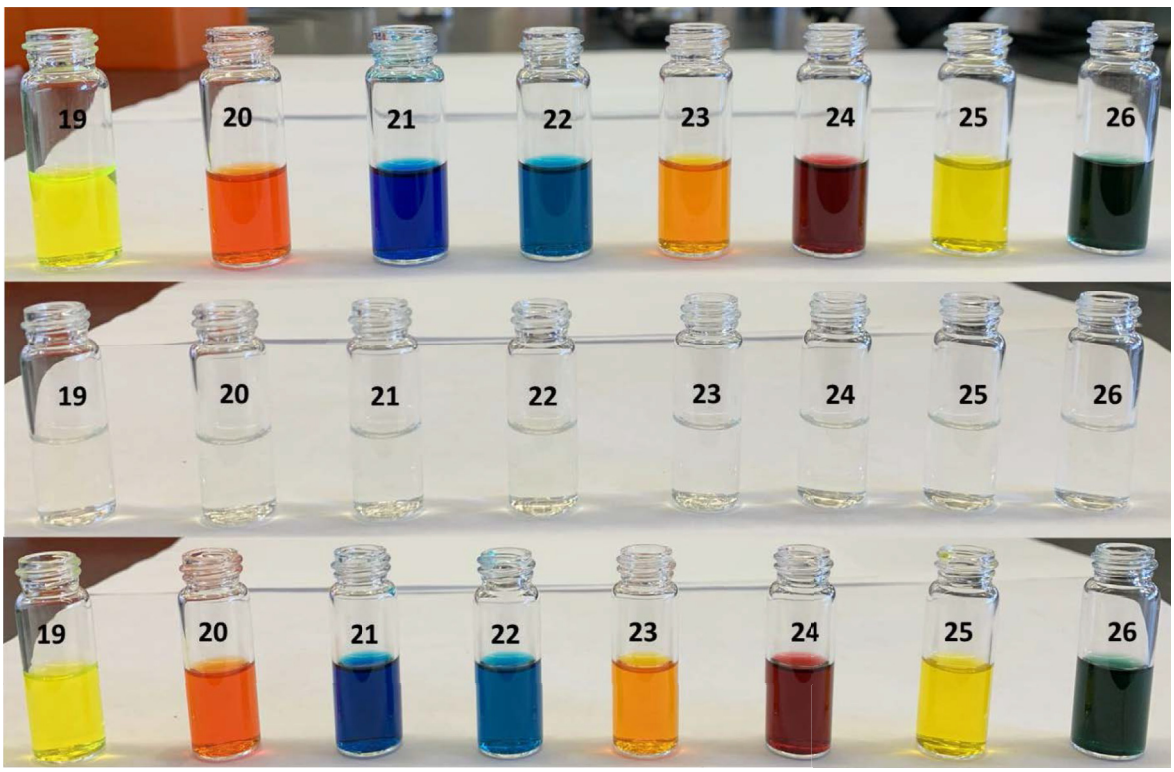

Fig. 3. Photographs of 9-aryldibenzo[b,e]pyrylium salts **19**–**26** in solution. **Top**: Vials containing 2 mL solutions of **19**–**26**, 1.0 mM in CH_3CN. **Middle**: Vials from the top after addition of 80 μL of TEA. **Bottom**: Vials from the middle after addition of 200 μL of TFA.

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containing donor-acceptor compounds relative to similar monophenyl donor-acceptor compounds [34]. Since the dimethylamino groups of **16** and **25** are further removed from and less conjugated to the strongly electron withdrawing pyrylium unit by a biphenyl spacer, instead of a monophenyl spacer (**12** and **21**), they are more basic and readily protonated by the strong acids required for pyrylium formation. In order to attempt to attenuate the stronger basicity of the dimethyl amino group in **16** and **25**, **17** and **26** with diphenylamino donor units and biphenyl spacers were synthesized. The diphenylamino group allows for further delocalization of the amine lone pair which reduces its basicity. Diphenylamino-donor containing pyrylium salts with monophenyl spacers (**13** and **22**) were also synthesized for direct comparison. The diphenylamino group does reduce the basicity of the amino group as is evidenced by the bright blue (**17**) and green (**26**) color of their solutions. However, based on UV–vis and NMR spectral data, discussed below, we believe these compounds are still partially protonated.

We have previously demonstrated the halochromism of pyrylium salts **10**–**12** in organic solution. This feature is now seen to be generally extended to a wide array of benzannulated pyrylium salts, as all compounds in this study (**10**–**17** and **19**–**26**) display highly visual halochromism (Figs. 2 and 3). These compounds are only soluble in organic solution and thus halochromism was demonstrated with the organic soluble acids and bases, trifluoroacetic acid (TFA) and triethylamine (TEA). Compounds **10**–**17** and **19**–**26** when dissolved 1.0 mM in CH_3CN could all be made colorless directly upon addition of excess TEA. Their colors could then return directly upon excess addition of TFA. The highly acid sensitive salts **16** and **25** both began yellow before TEA addition and then returned to yellow after TFA addition. However, **25** did display fleeting light green yellow coloring during the addition process.

2.3. Spectroscopic characterization and comparison

All pyrylium salts were also probed by UV–vis spectroscopy (Fig. 4 and Table 1) and the trends observed by visual inspection are observed spectroscopically as well. In comparing the dibenzo[b,d]pyrylium **10**–**17** containing salts with the analogous xanthylium **19**–**26** salts we see clear evidence of a bathochromic shift for the xanthylium compounds, which is weaker in those compounds containing only unsubstituted aryl units and more pronounced is those with donor substituents. This can be at least partially attributed to the longer distance between the donor unit and the oxonium cation of the pyrylium unit in the xanthylium containing compounds compared to the dibenzo[b,d]pyrylium compounds. Comparison of **16** and **25** show only a small difference in highest wavelength absorbed, providing evidence of protonation, because the protonation of the amino unit would not allow for appreciable donation into the oxonium acceptor. Another trend that can be observed is that the molar absorptivity of the unprotonated donor-containing dibenzo[b,d]pyrylium compounds (**11**–**13**, **15**) is larger than the analogous xanthylium compounds (**20**–**22**, **24**) (Table 1). We believe this to be impacted by the structural differences between the aryl spacers on the two isomeric units. It would be assumed that the conjugated aryl spacers could achieve better pi-orbital overlap in the dibenzo[b,d]pyrylium compounds due to less steric demand of what is effectively a mono-ortho substituted aryl-aryl bond between the spacer and the dibenzo[b,d]pyrylium acceptor subunit. The xanthylium compounds should have larger dihedral angles between the aryl spacer units and the di-ortho substituted xanthylium acceptor subunit. This would result in more effective conjugation for the compounds containing the dibenzo[b,d]pyrylium unit between the donor and oxonium acceptor.

To further probe the effect of structure on the observed optical properties, crystals of dibenzo[b,d]pyrylium **10** and xanthylium **23** were grown that were suitable for X-ray crystallography. At the time of this writing, crystals of **14** or **19** with sufficient quality for X-ray analysis were not achieved after numerous attempts. Regardless, the X-ray crystallographic data (see supplementary data) support our hypothesis: the average aryl-aryl dihedral between the aryl spacer and dibenzo[b,d]pyrylium subunit of **10** was found to be 36(1)° whereas the analogous aryl-xanthylium dihedral for **23** was 56.2(4)°, with each dihedral listed with the estimated standard deviation (esd) in parentheses. Therefore, there is a significant structural variation between the two isomers with aryl-aryl dihedrals differing by approximately 20° in the crystalline state. The structure in the crystalline state of dibenzo[b,d]pyrylium subunit is more favorable for extended conjugation when compared to that of the isomeric xanthylium.

The UV–vis spectra (Fig. 4 and Table 1) expectedly show large bathochromic shifts for those compounds containing amino-donors (unprotonated) compared to the weaker methoxy donors or those containing no donor groups due to stronger intramolecular charge transfer (ICT). The monophenyl and analogous biphenyl spacer containing compounds can also be directly compared. The donor-acceptor biphenyl spacer containing compounds were expected to be red-shifted due to the longer conjugation pathway but also have lower molar absorptivity due to less effective conjugation inherent in cumulative aryl-aryl torsions, relative to the analogous monophenyl spacer compounds [34]. This effect is the clearest when comparing the methoxy-containing compounds **11** (monophenyl) and **15** (biphenyl) or **20** (monophenyl) and **24** (biphenyl). The amino containing compounds are more susceptible to protonation in the biphenyl-spacer containing compounds and a direct comparison to their monophenyl analogs is less useful. However, it is clear that the absorption is highly dependent on the identity of the spacer unit in the amino-containing compounds.

It is evident from the yellow color upon visual inspection and lack of ICT band in the UV–vis spectra that **16** and **25** are protonated at the dimethylamino unit. However, the degree of protonation of the diphenylamino unit on **17** and **26** appears to be reduced relative to **16** and **25**. There is clearly donor-acceptor character in **17** and **26** as evidenced by visual inspection of their color (blue and green). In their UV–vis spectra, compounds **17** and **26** both have a measurable ICT band, but it is greatly attenuated relative to monophenyl-spacer analogs **13** and **22**. Conversely, comparison of the ICT band for monophenyl and biphenyl methoxy substituted **11**/**20** and **15**/**24** shows a less pronounced attenuation of absorption. It is also apparent from ^{1}H NMR data (see supplementary data) of **17** and **26** that the phenyl protons on the diphenylamino unit are broadened. These broad peaks in the ^{1}H NMR data suggests that proton-transfer equilibration is occurring at the amine moiety.

In addition to UV–vis data, observed ^{13}C NMR chemical shifts of the pyrylium C6 atoms in **10**–**17** and the pyrylium C9 atoms in **19**–**26** illuminates the degree of donor unit delocalization into the oxonium acceptor (Table 2 and supplementary data). Chemical shifts of pyrylium compounds containing monophenyl spacers (**10**–**13** and **19**–**22**) vary considerably depending on the identity of the substituent on the aryl group, with the amino donor substituents causing the greatest upfield shift. Conversely, those containing biphenyl spacers (**14**–**17** and **23**–**26**) have similar chemical shifts, most approaching that of unsubstituted monophenyl spacer containing **10** and **19**, regardless of donor identity. Once again, this illustrates that the donor unit held further away from to the oxonium acceptor and subject to cumulative torsions, is less delocalized, consistent with UV–vis data. A direct comparison of monophenyl spacer containing dibenzo[b,d]pyrylium compounds **10**–**13** with monophenyl spacer containing xanthylium compounds **19**–**22** can also be done. The observed ^{13}C chemical shifts of

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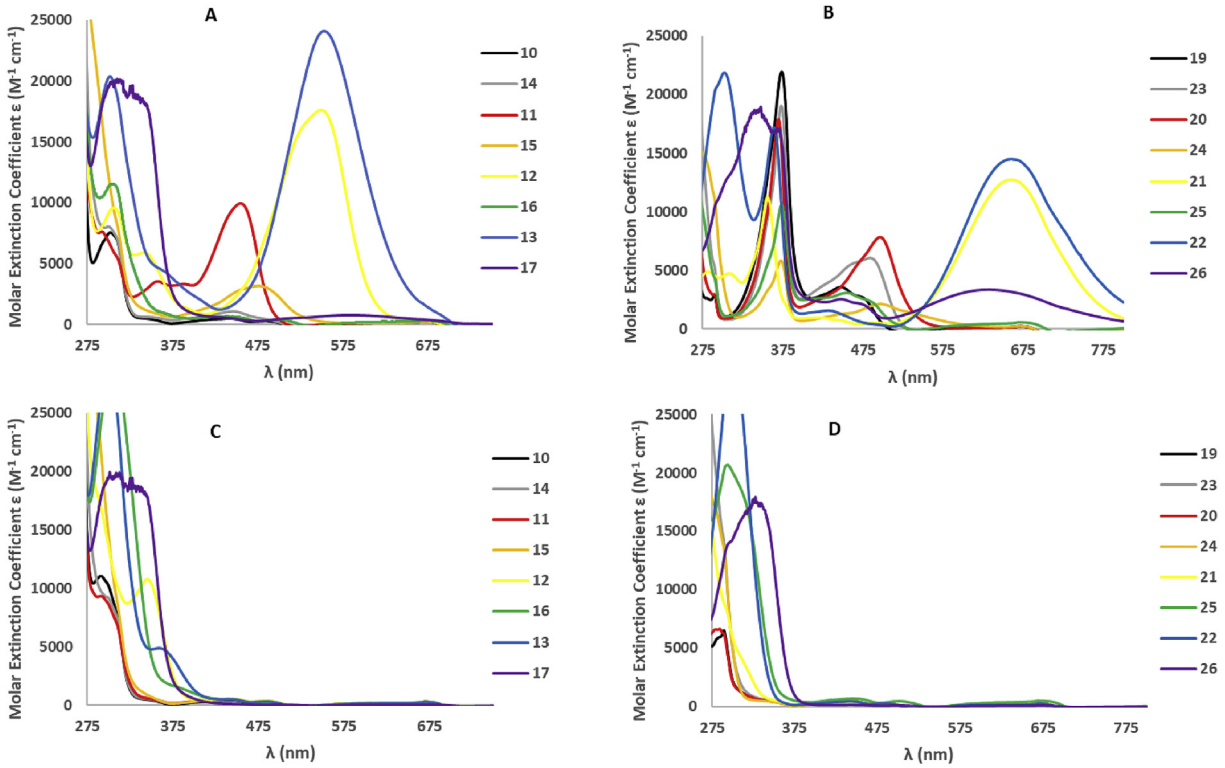

Fig. 4. UV−vis spectra for: (A) **10**–**17** 30.0 μM in CH_3CN; (B) **19**–**26** 30.0 μM in CH_3CN; (C) samples from (A) after addition of 1 drop of TEA; (D) samples from (B) after addition of 1 drop of TEA.

Table 1
UV−vis absorption data for **10**–**17** and **19**–**26** 30.0 μM in CH_3CN.

compd	lowest E abs λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])	compd	lowest E abs λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])
10	440 (483)	**19**	447 (3618)
11	452 (9912)	**20**	496 (7878)
12	549 (17607)	**21**	660 (12741)
13	552 (24095)	**22**	660 (14510)
14	444 (1100)	**23**	484 (6057)
15	476 (3204)	**24**	498 (2159)
16	445 (658)	**25**	454 (3133)
17	583 (760)	**26**	633 (3394)

Table 2
Observed ^{13}C NMR chemical shifts (δ) of C6 for **10**–**17** and C9 for **19**–**26**. All were dissolved in $CDCl_3$ with added CF_3CO_2D except* **17**, **21**, and **26** which were dissolved in CD_2Cl_2 with no added CF_3CO_2D, due to proton sensitivity.

compd	δ (ppm)	compd	δ (ppm)
10	184.9	**19**	175.4
11	182.4	**20**	174.6
12	178.5	**21***	168.4
13	177.2	**22**	170.8
14	183.8	**23**	175.2
15	183.7	**24**	174.9
16	184.2	**25**	175.2
17*	183.4	**26***	175.3

10–**13** at C6 vary by 7.7 ppm, whereas the observed ^{13}C chemical shifts of **19**–**22** at C9 vary only by 4.6 ppm (not accounting for data from **21**, which is not directly comparable since it was collected dissolved in CD_2Cl_2 with no added TFA due to acid sensitivity). This is again in agreement with UV−vis data which showed that the donor unit has more effect on ICT in dibenzo[b,d]pyrylium compounds compared to isomeric xanthylium compounds.

Finally, the halochromism of these pyrylium compounds is also readily observed in the UV−vis data (Fig. 4). UV−vis spectra of pyrylium compounds dissolved in CH_3CN are shown in Fig. 4A and B. A drop of TEA was added to the samples from 4A to 4B and the subsequent UV−vis spectra are seen in 4C and 4D. In all cases the ICT bands have diminished and a general hypsochromic shift is observed. This is consistent with the visual observations shown in Figs. 2 and 3.

3. Conclusions

A library of isomeric dibenzopyrylium salts containing either 6-aryldibenzo[b,d]pyrylium or 9-aryldibenzo[b,e]pyrylium (9-arylxanthylium) subunits were synthesized and their optical properties were directly compared. Prior to this study, compounds containing the 6-aryldibenzo[b,d]pyrylium subunit were quite rare and poorly studied, despite the related flavylium cation being a very common naturally-occurring colorant. Compounds containing

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the 9-arylxanthylium cation with no further substitution and the xanthylium unit are also surprisingly rare, despite their substituted analogs being commonly featured in popular rhodamine and rosamine dyes. In this study, eleven new dibenzopyrylium compounds have been synthesized, isolated and characterized (**13**–**17**, **21**–**26**). These were all compared with known pyrylium compounds **10**–**12,** and **19**–**20**. We found that all dibenzopyrylium salts synthesized for this study displayed a variety of attractive bright colors that were directly dependent on 1) the isomeric structure of the dibenzopyrylium subunit, 2) the presence and identity of a donor unit on the appended aryl moiety, 3) the use of either a monophenyl or biphenyl spacer between the donor unit and pyrylium acceptor, and 4) if present, further protonation at the amino donor group. All compounds studied demonstrated reversible halochromism in organic solution with color being visible in acidic environments and absent in basic environments. This study reveals that the optical properties of dibenzopyrylium salts can be directly engineered by simple modular synthetic manipulation of molecular structure resulting in an impressive array of possible colors.

4. Experimental section

4.1. General comments

Reactants **4** [37], **6** [38], **7** [39], **8** [40], and **9** [28] were prepared via reported literature methods. All other reactants, reagents, and solvents were purchased commercially and used without further purification. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 (100) MHz instrument. Chemical shifts are reported in parts per million (ppm) and referenced to the appropriate residual solvent peak. All IR spectra were recorded with a Thermo Scientific Nicolet I5S FT-IR spectrometer with ATR. UV–Vis spectroscopy was performed with a Cary 50 spectrophotometer using 1 cm quartz cells. High resolution mass spectrometry was performed with an Agilent 6210 Time of Flight LC/MS. Purification by column chromatography was performed using a Biotage Isolera One flash chromatography system and Biotage SNAP KP-Sil cartridges. Melting points were obtained with a Mel-Temp electrothermal melting point apparatus. Diffraction data was collected with a Rigaku XtaLAB Mini II benchtop X-ray diffractometer. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication 1989521 and 1989522 CCDC. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223–336033 or e-mail: deposit@ccdc.cam.ac.Uk).

4.2. 6-(4-(Diphenylamino)phenyl)benzo[c]chromen-5-ium tetrafluoroborate (*13*)

4-bromotriphenylamine **4** (1.50 g, 4.63 mmol) was dissolved in 20 mL of anhydrous THF in an oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. 1.6 M n-BuLi in hexane (3.48 mL, 5.57 mmol) was added dropwise via syringe and the reaction was stirred for 1 h at −78 °C. During this time 6H-benzo[c]chromen-6-one **9** (0.910 g, 4.63 mmol) was dissolved in 20 mL of anhydrous THF in a separate oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. The aryllithium solution was transferred to the solution containing **9** at −78 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was allowed to stir for 2 h. The reaction was poured into 150 mL of sat. NH_4Cl and extracted 3x with 75 mL of EtOAc. The combined organics were washed 2x with 70 mL of H_2O and 2x with 70 mL of brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was dissolved in 10 mL of diethyl ether in a round bottom flask and cooled to 0 °C with an ice bath. While stirring rapidly the solution, 3 mL of acetic anhydride and 10 drops of 48% aq. HBF_4 was added. The reaction was allowed to stir for 1 h and filtered to yield a dark green/black solid that was not purified further (994 mg, 42%). mp 213–215 °C. ^{1}H NMR (400 MHz, $CDCl_3/CF_3CO_2D$): δ 8.66 (d, $J = 8.3$ Hz, 1H), 8.61 (d, $J = 8.3$ Hz, 1H), 8.51 (d, $J = 8.3$ Hz, 1H), 8.33 (t, $J = 7.3$ Hz, 1H), 8.19 (d, $J = 9.3$ Hz, 2H), 7.99-7.93 (m, 3H), 7.85-7.80 (m, 1H), 7.54 (t, $J = 7.7$ Hz, 4H), 7.44 (t, $J = 7.3$ Hz, 2H), 7.36 (d, $J = 7.8$ Hz, 4H), 7.16 d, $J = 9.0$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3/CF_3CO_2D$): δ 177.2, 157.3, 150.2, 143.2, 140.6, 137.1, 136.9, 134.6, 133.6, 131.1, 130.5, 129.2, 128.4, 127.0 123.52, 123.47, 121.3, 119.3, 119.1, 118.7, 118.5. IR (ATR) ν_{max}: 1580, 1552, 1046 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{31}H_{22}NO$ [M+] 424.1701, found 424.1691.

4.3. 6-([1,1′-Biphenyl]-4-yl)benzo[c]chromen-5-ium perchlorate (*14*)

Magnesium (0.190 g, 7.50 mmol) was placed into an oven-dried round bottom flask and flushed with Ar for 30 min while stirring. 4-Bromobiphenyl **5** (1.75 g, 7.50 mmol), anhydrous THF (10 mL), and a crystal of I_2 were then added and the reaction stirred for 1.5 h under Ar. During this time 6H-benzo[c]chromen-6-one **9** (0.981 g, 5.00 mmol) was dissolved in 10 mL of anhydrous THF in a separate oven dried round bottom flask. The flask was cooled to 0 °C with an ice bath and sparged for 30 min with Ar. The arylmagnesium bromide solution was transferred to the solution containing **9** at 0 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was stirred for 18 h. 50 mL of sat. NH_4Cl was added to the reaction and subsequently extracted 3x with 25 mL of Et_2O. The combined organics were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was dissolved in 25 mL of diethyl ether and cooled to 0 °C in an ice bath and stirred very rapidly. A chilled (0 °C) solution of 70% perchloric acid in acetic anhydride (1:3 by volume) was slowly added drop-wise to the stirring ethereal solution until a colored precipitate formed. The crude product was filtered and recrystallized in glacial acetic acid to yield orange-yellow needles (1.36 g, 63%). mp 234–236 °C. ^{1}H NMR (400 MHz, $CDCl_3/CF_3CO_2D$): δ 8.93 (d, $J = 8.3$ Hz, 1H), 8.87 (d, $J = 8.3$ Hz, 1H), 8.79 (d, $J = 8.3$ Hz, 1H), 8.61 (t, $J = 8.3$ Hz, 1H), 8.36 (d, $J = 8.5$ Hz, 2H), 8.29 (d, $J = 8.5$ Hz, 1H), 8.20-8.04 (m, 5H), 7.80-7.77 (m, 2H), 7.61-7.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3/CF_3CO_2D$): δ 183.8, 151.5, 150.0, 143.9, 139.6, 138.1, 136.2, 134.6, 134.2, 132.0, 130.8, 129.8, 129.4, 128.6, 127.9, 127.6, 123.1, 123.9, 121.5, 120.6, 119.9. IR (ATR) ν_{max}: 1597, 1542, 1069 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{25}H_{17}O$ [M+] 333.1279, found 333.1276.

4.4. 6-(4′-Methoxy-[1,1′-biphenyl]-4-yl)benzo[c]chromen-5-ium perchlorate (*15*)

4-bromo-4′-methoxybiphenyl **6** (0.671 g, 2.55 mmol) was dissolved in 10 mL of anhydrous THF in an oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 45 min. 1.6 M n-BuLi in hexane (1.70 mL, 2.72 mmol) was added dropwise via syringe and the reaction was stirred for 1.5 h at −78 °C. During this time 6H-benzo[c]chromen-6-one **9** (0.500 g, 2.55 mmol) was dissolved in 10 mL of anhydrous THF in a separate oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. The aryllithium solution was transferred to the solution containing **9** at −78 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was allowed to stir for 2 h. 50 mL of sat. NH_4Cl was added to the reaction and subsequently

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extracted 3x with 25 mL of Et_2O. The combined organics were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was dissolved in 25 mL of diethyl ether and cooled to 0 °C in an ice bath and stirred very rapidly. A chilled (0 °C) solution of 70% perchloric acid in acetic anhydride (1:3 by volume) was slowly added drop-wise to the stirring ethereal solution until a colored precipitate formed. The crude product was filtered and recrystallized in glacial acetic acid to yield a red-orange powder (0.508 g, 43%). mp 270–271 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3CO_2D): δ 8.90 (d, J = 8.5 Hz, 1H), 8.86 (d, J = 8.5 Hz, 1H), 8.76 (dd, J = 8.3 Hz, J = 1.5 Hz, 1H), 8.59 (t, J = 7.9 Hz, 1H), 8.36 (d, J = 8.5 Hz, 2H), 8.27 (dd, J = 8.4 Hz, J = 1.1 Hz, 1H), 8.17 (t, J = 8.3 Hz, 1H), 8.12 (td, J = 7.9 Hz, J = 1.5 Hz, 1H), 8.07-8.01 (m, 3H), 7.77 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ 183.7, 160.6, 151.6, 150.2, 143.9, 139.7, 136.2, 134.9, 134.3, 132.1, 131.2, 131.0, 129.2, 128.2, 127.3, 124.1, 124.0, 121.5, 120.5, 119.8, 115.3, 55.9. IR (ATR) ν_{max}: 1592, 1483, 1078 cm^{-1}. HRMS (ESI) m/z calcd for $C_{26}H_{19}O_2$ [M+] 363.1385, found 363.1373.

4.5. 6-(4'-(Dimethylamino)-[1,1′-biphenyl]-4-yl)benzo[c]chromen-5-ium tetrafluoroborate (**16**)

Magnesium (0.156 g, 6.40 mmol) was placed into an oven-dried round bottom flask and flushed with Ar for 30 min while stirring. 4′-Bromo-4-dimethylaminobiphenyl **7** (1.45 g, 5.23 mmol), anhydrous THF (25 mL), and 2 drops of 1,2-dibromoethane were then added. The reaction was heated to reflux and stirred for 16 h under Ar. During this time 6H-benzo[c]chromen-6-one **9** (0.802 g, 4.09 mmol) was dissolved in 35 mL of anhydrous THF in a separate oven dried round bottom flask. The flask was cooled to 0 °C with an ice bath and sparged for 30 min with Ar. The arylmagnesium bromide solution was transferred to the solution containing **9** at 0 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was stirred for 18 h. 25 mL of sat. NH_4Cl was added to the reaction and subsequently extracted 4x with 25 mL of Et_2O. The combined organics were washed 2x with 75 mL of H_2O, dried with $CaCl_2$, filtered, and concentrated under reduced pressure. The crude intermediate was purified via column chromatography using gradient elution (hexane →20% EtOAc in hexane) but not characterized further. The purified intermediate was dissolved in 10 mL of diethyl ether and cooled to 0 °C in an ice bath and stirred rapidly. While stirring rapidly the solution, 3 mL of acetic anhydride and 48% aq. HBF_4 was added until precipitation, likely protonated at the amino group. The reaction was allowed to stir for 1 h and filtered to yield an orange-yellow solid (0.228 g, 12%). The product was only able to be isolated in its protonated form was therefore analyzed via NMR spectroscopy dissolved in CD_3Cl as a solvent with added CF_3CO_2D, which improved its solubility. mp 238–239 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3CO_2D): δ 8.95 (d, J = 8.8 Hz, 1H), 8.89 (d, J = 8.8 Hz, 1H), 8.80 (d, J = 7.8 Hz, 1H), 8.65 (t, J = 7.8 Hz, 1H), 8.38 (d, J = 7.8 Hz, 2H), 8.34 (d, J = 8.8 Hz, 1H), 8.23-8.17 (m, 2H), 8.13-8.09 (m, 3H), 7.89 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 3.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ 184.2, 152.0, 147.7, 144.8, 142.5, 141.7, 140.4, 136.2, 135.5, 134.0, 132.5, 131.6, 130.3, 129.2, 129.1, 124.2, 124.1, 121.6, 121.2, 120.8, 120.0, 47.9. IR (ATR) ν_{max}: 1597, 1544, 1071 cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{22}NO$ [M+] 376.1701, found 376.1687.

4.6. 6-(4'-(Diphenylamino)-[1,1′-biphenyl]-4-yl)benzo[c]chromen-5-ium tetrafluoroborate (**17**)

4′-Bromo-N,N-diphenyl-[1,1′-biphenyl]-4-amine **8** (1.60 g, 4.00 mmol) was dissolved in 25 mL of anhydrous THF in an oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 20 min. 2.5 M n-BuLi in hexane (1.60 mL, 4.00 mmol) was added dropwise via syringe and the reaction was stirred for 15 min at −78 °C. The cooling bath was removed, and the reaction stirred for 10 min. The reaction was cooled back to −78 °C and stirred another 15 min. During this time 6H-benzo[c]chromen-6-one **9** (713 mg, 3.63 mmol) was dissolved in 10 mL of anhydrous THF in a separate oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 10 min. The aryllithium solution was transferred to the solution containing **9** at −78 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction stirred for 10 min. The reaction was cooled back to −78 °C and stirred another 15 min. The reaction was quenched by the addition of 20 mL of sat. NH_4Cl over 10 min at −78 °C. The cooling bath was removed, and the reaction was allowed to warm to rt with stirring. 20 mL of water was added, and the mixture was subsequently extracted 3x with 50 mL of EtOAc. The combined organics were washed with brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure to yield a crude oily solid. The crude product was purified with column chromatography under gradient elution (10:90 CH_2Cl_2:hexane → 80:20 CH_2Cl_2:hexane) to yield **17a** as a light-yellow powder (750 mg, 40%) but not characterized further. 300 mg (0.580 mmol) of **17a** was dissolved in 20 mL of CH_2Cl_2 in a graduated cylinder and 0.1 mL of a neat 1:1 HBF_4 diethyl ether complex and 0.5 mL of Ac_2O was carefully added resulting in a blue solution. Diethyl ether (30 mL) was layered on top of the solution and was allowed to sit for 48 h as a ppt formed. The ppt was filtered to achieve a greenish/black solid (273 mg, 80%). The product was acid sensitive and was therefore analyzed via NMR spectroscopy dissolved in CD_2Cl_2 as a solvent with no added CF_3CO_2D, which reduced its solubility. mp 226–229 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.92 (d, J = 8.6 Hz, 1H), 8.84 (d, J = 8.3 Hz, 1H), 8.78 (d, J = 8.1 Hz, 1H), 8.60 (t, J = 7.7 Hz, 1H), 8.36 (d, J = 8.6 Hz, 2H), 8.27 (d, J = 8.3 Hz, 1H), 8.17 (t, J = 7.8 Hz, 1H), 8.15-8.02 (m, 4H), 7.73 (br, 2H), 7.36 (br, 5H) 7.20 (br, 7H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 183.4, 151.9, 144.1, 139.8, 136.5, 135.2, 135.1, 132.6, 131.2, 130.2, 129.1, 128.2, 127.5, 126.3, 124.7, 124.6, 124.1, 122.1, 121.0, 120.3. IR (ATR) ν_{max}: 1583, 1485, 1050 cm^{-1}. HRMS (ESI) m/z calcd for $C_{37}H_{26}NO$ [M+] 500.2014, found 500.2023.

4.7. 9-(4-(dimethylamino)phenyl)xanthylium tetrafluoroborate (**21**)

4-Bromo-N,N-dimethylaniline **3** (1.00 g, 4.98 mmol) was dissolved in 30 mL of anhydrous THF in an oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. 1.6 M n-BuLi (3.75 mL, 6.00 mmol) was added dropwise and the reaction was stirred for 1 h at −78 °C. During this time xanthone **18** (981 mg, 5.00 mmol) was dissolved in 50 mL of anhydrous THF in a separate oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. The aryllithium solution was transferred to the solution containing **18** at −78 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was stirred for 4 h. The reaction was quenched with 75 mL sat. NH_4Cl. The mixture was subsequently extracted 3x with 50 mL of EtOAc. The combined organics were washed with brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure to yield a highly acid-sensitive crude yellow/brown solid. The crude product was purified via column chromatography (5% EtOAc in hexane →50% EtOAc in hexane, both solvents containing 1% triethylamine) to obtain **21a** as a yellow powder (560 mg, 35%) but not characterized further. 215 mg (0.677 mmol) of **21a** was dissolved in 12 mL of CH_2Cl_2 in a graduated cylinder and 0.1 mL of a neat 1:1 HBF_4 diethyl ether complex was carefully added resulting in a blue

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solution. Diethyl ether (35 mL) was layered on top of the solution and was allowed to sit for 48 h as a ppt formed. The ppt was filtered to achieve a red/purple solid (109 mg, 42%). The product was acid sensitive and was therefore analyzed via NMR spectroscopy dissolved in CD_2Cl_2 as a solvent with no added CF_3CO_2D, which reduced its solubility. mp 156–158 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.32 (dd, J = 8.6 Hz, 1.2 Hz, 2H), 8.23 (t, J = 8.0 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H), 7.84-7.80 (m, 4H), 7.14 (d, J = 9.3 Hz, 2H), 3.35 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 168.4, 156.9, 156.3, 140.7, 138.0, 133.3, 128.4, 122.7. 121.3, 119.9, 114.1, 41.1. IR (ATR) ν_{max}: 1595, 1465, 1050 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{18}NO$ [M+] 300.1388, found 300.1401.

4.8. 9-(4-(diphenylamino)phenyl)xanthylium tetrafluoroborate (**22**)

4-Bromotriphenylamine **4** (2.48 g, 7.64 mmol) was dissolved in 30 mL of anhydrous THF in an oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. 1.6 M n-BuLi in hexane (5.80 mL, 9.28 mmol) was added dropwise via syringe and the reaction was stirred for 1 h at −78 °C. During this time xanthone **18** (1.50 g, 7.64 mmol) was dissolved in 40 mL of anhydrous THF in a separate oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. The aryllithium solution was transferred to the solution containing **18** at −78 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was allowed to stir for 2 h. The reaction was poured into 150 mL of sat. NH_4Cl and extracted 3x with 75 mL of EtOAc. The combined organics were washed 2x with 70 mL of H_2O and 2x with 70 mL of brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was dissolved in 10 mL of diethyl ether in a round bottom flask and cooled to 0 °C with an ice bath. While stirring rapidly the solution, 3 mL of acetic anhydride and 10 drops of 48% aq. HBF_4 was added. The reaction was allowed to stir for 1 h and filtered to yield a blue-green solid that was not purified further (1.68 g g, 43%). mp 272–273 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3CO_2D): δ 8.40–8.44 (m, 4H), 8.17 (d, J = 8.8 Hz, 2H), 7.89 (t, J = 7.7 Hz, 2H), 7.67, (d, J = 8.8 Hz, 2H), 7.53-7.49 (m, 4H), 7.39-7.35 (m, 6H), 7.28 (d, J = 8.6, Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ 170.8, 157.2, 154.7, 144.3, 141.8, 136.0, 132.3, 130.4, 128.6, 127.4, 127.1, 122.6, 122.5, 119.7 118.5. IR (ATR) ν_{max}: 1597, 1567, 1064 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{31}H_{22}NO$ [M+] 424.1701, found 424.1692.

4.9. 9-([1,1′-biphenyl]-4-yl)xanthylium perchlorate (**23**)

Magnesium (0.389 g, 16.2 mmol) was placed into an oven-dried round bottom flask and flushed with Ar for 30 min while stirring. 4-Bromobiphenyl **5** (3.73 g, 16.0 mmol), anhydrous THF (20 mL), and 2 drops of 1,2-dibromoethane were then added. The reaction was heated to reflux, stirred for 30 min under Ar, and allowed to cool back to rt over 1 h. During this time xanthone **18** (1.54 g, 7.85 mmol) was dissolved in 50 mL of anhydrous THF in a separate oven dried round bottom flask. The flask was cooled to 0 °C with an ice bath and sparged for 30 min with Ar. The arylmagnesium bromide solution was transferred to the solution containing **18** at 0 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was stirred for 2 h. 50 mL of sat. $NaHCO_3$ was added to the reaction and subsequently extracted 3x with 100 mL of CH_2Cl_2. The combined organics were washed dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude intermediate was purified via column chromatography using gradient elution (5% EtOAc in hexane →50% EtOAc in hexane) but not characterized further. The purified intermediate was dissolved in 10 mL of diethyl ether and 70% aq. $HClO_4$ was added dropwise at rt until a colored precipitate formed. The reaction was allowed to stir for 1 h and filtered to yield an orange solid. The solid was recrystallized in glacial acetic acid to yield small orange needles (1.73 g, 51%). mp 266–267 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3CO_2D): δ 8.55 (t, J = 8.8 Hz, 2H), 8.42 (d, J = 8.3 Hz, 2H), 8.32 (dd, J = 8.7 Hz, J = 1.6, 2H), 8.05 (d, J = 8.3 Hz, 2H), 7.99 (t, J = 8.8 Hz, 2H), 7.81-7.76 (m, 4H), 7.59 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ 175.2, 158.5, 146.4, 144.3, 138.8, 132.0, 131.6, 129.6, 129.4, 129.2, 128.1, 127.4, 123.6, 120.1. IR (ATR) ν_{max}: 1599, 1578, 1088 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{25}H_{17}O$ [M+] 333.1279, found 333.1270.

4.10. 9-(4′methoxy-[1,1′-biphenyl]-4-yl)xanthylium perchlorate (**24**)

Magnesium (0.132 g, 5.42 mmol) was placed into an oven-dried round bottom flask and flushed with Ar for 30 min while stirring. 4-Bromo-4′-methoxybiphenyl **6** (1.43 g, 5.42 mmol), anhydrous THF (8 mL), and 2 drops of 1,2-dibromoethane were then added. The reaction was heated to reflux, stirred for 30 min under Ar, and allowed to cool back to rt over 1 h. During this time xanthone **18** (0.532 g, 2.71 mmol) was dissolved in 16 mL of anhydrous THF in a separate oven dried round bottom flask. The flask was cooled to 0 °C with an ice bath and sparged for 30 min with Ar. The arylmagnesium bromide solution was transferred to the solution containing **18** at 0 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction was stirred for 2 h. 50 mL of sat. $NaHCO_3$ was added to the reaction and subsequently extracted 3x with 100 mL of CH_2Cl_2. The combined organics were washed dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude intermediate was purified via column chromatography using gradient elution (5% EtOAc in hexane →50% EtOAc in hexane) but not characterized further. The purified intermediate was dissolved in 10 mL of diethyl ether and 70% aq. $HClO_4$ was added dropwise at rt until a colored precipitate formed. The reaction was allowed to stir for 30 min and filtered to yield a red solid. The solid was recrystallized in glacial acetic acid to yield small red needles (0.595 g, 47%). mp 230–231 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3CO_2D): δ 8.51 (ddd, J = 8.6 Hz, J = 7.0 Hz, J = 1.2 Hz, 2H), 8.37 (d, J = 8.8 Hz, 2H) 8.33 (dd, J = 8.7 Hz, J = 1.3 Hz, 2H), 8.01-7.94 (m, 4H), 7.78 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H) 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ 174.9, 160.2, 158.3, 145.7, 144.0, 132.0, 131.9, 131.4, 129.4, 128.7, 128.6, 127.3, 123.5, 120.0, 114.8, 55.6. IR (ATR) ν_{max}: 1596, 1578, 1083 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{26}H_{19}O_2$ [M+] 363.1385, found 363.1382.

4.11. 9-(4′-(dimethylamino)-[1,1′-biphenyl]-4-yl)xanthylium perchlorate (**25**)

4′-Bromo-4-dimethylaminobiphenyl **7** (1.70 g, 6.14 mmol) was dissolved in 50 mL of anhydrous THF in an oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. 1.6 M n-BuLi in hexane (5.00 mL, 8.00 mmol) was added dropwise via syringe and the reaction was stirred for 30 min at −78 °C. During this time xanthone **18** (1.21 mg, 6.14 mmol) was dissolved in 30 mL of anhydrous THF in a separate oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. The

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aryllithium solution was transferred to the solution containing **18** at −78 °C via cannula under Ar pressure and stirred for 2 h. The cooling bath was removed, and the reaction stirred while warming to rt. The reaction was quenched by the addition of 150 mL of sat. NH_4Cl. The mixture was subsequently extracted 3x with 75 mL of EtOAc. The combined organics were washed with brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure to yield a crude solid. The purified intermediate was dissolved in 10 mL of diethyl ether and 70% aq. $HClO_4$ was added dropwise at rt until a colored precipitate formed. The reaction was allowed to stir for 30 min and filtered to yield a yellow/brown. The solid was recrystallized in glacial acetic acid and acetic anhydride to yield a yellow powder (0.789 g, 27%). The product was only able to be isolated in its protonated form was therefore analyzed via NMR spectroscopy dissolved in $CDCl_3$ as a solvent with added CF_3CO_2D, which improved its solubility. mp 277–278 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3CO_2D): δ 8.59 (t, J = 7.8 Hz, 2H), 8.42 (d, J = 8.8 Hz, 2H), 8.33 (d, J = 8.6 Hz, 2H), 8.07-7.98 (m, 6H), 7.83 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 3.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ 175.2, 158.7, 144.8, 143.8, 142.4, 141.9, 132.1, 131.7, 130.5, 130.2, 130.0, 128.5, 123.8, 121.1, 120.1, 48.0. IR (ATR) ν_{max}: 1598, 1579, 1087 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{27}H_{22}NO$ [M+] 376.1701, found 376.1692.

4.12. 9-(4′-(diphenylamino)-[1,1′-biphenyl]-4-yl)xanthylium tetrafluoroborate (**26**)

4′-Bromo-N,N-diphenyl-[1,1′-biphenyl]-4-amine **8** (1.00 g, 2.50 mmol) was dissolved in 20 mL of anhydrous THF in an oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 20 min. 1.6 M n-BuLi in hexane (1.88 mL, 3.00 mmol) was added dropwise via syringe and the reaction was stirred for 1 h at −78 °C. During this time xanthone **18** (490 mg, 2.50 mmol) was dissolved in 30 mL of anhydrous THF in a separate oven dried round bottom flask. The solution was cooled to −78 °C in a dry ice/acetone bath and sparged with Ar for 30 min. The aryllithium solution was transferred to the solution containing **18** at −78 °C via cannula under Ar pressure. The cooling bath was removed, and the reaction stirred for 4 h. The reaction was quenched by the addition of 75 mL of sat. NH_4Cl and the mixture was subsequently extracted 3x with 50 mL of EtOAc. The combined organics were washed with water and brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure to yield a crude solid. The crude product was purified with column chromatography under gradient elution (10:90 CH_2Cl_2:hexane → 80:20 CH_2Cl_2:hexane) to yield **26a** as a light-yellow powder (789 mg, 61%) which was not characterized further. 300 mg (0.580 mmol) of **16a** was dissolved in 20 mL of CH_2Cl_2 in a graduated cylinder and 0.1 mL of 1:1 HBF_4 diethyl ether complex and 0.5 mL of Ac_2O was carefully added resulting in a green solution. Diethyl ether (30 mL) was layered on top of the solution and was allowed to sit for 48 h as a ppt formed. The ppt was filtered to achieve a green solid (293 mg, 86%). The product was acid sensitive and was therefore analyzed via NMR spectroscopy dissolved in CD_2Cl_2 as a solvent with no added CF_3CO_2D, which reduced its solubility. mp 234–235 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.57 (t, J = 7.8 Hz, 2H), 8.41 (d, J = 8.8 Hz, 2H), 8.35 (d, J = 8.6 Hz, 2H), 8.05 (d, J = 7.8 Hz, 2H), 8.01 (t, J = 7.8 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.34 (t, J = 7.8 Hz, 4H), 7.21-7.17 (m, 6H), 7.13 (t, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 175.3, 158.5, 149.7, 147.7, 146.3, 144.7, 132.9, 132.7, 131.9, 130.0, 129.3, 128.6, 127.7, 125.8, 124.0, 123.2, 120.6. IR (ATR) ν_{max}: 1598, 1483, 1053 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{37}H_{26}NO$ [M+] 500.2014, found 500.2007.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131222.

References

[1] A.T. Balaban, W. Schroth, G. Fischer, Adv. Heterocycl. Chem. 10 (1969) 241–326.
[2] M. Nogradi, Sci. Synth. 14 (2003) 201–273.
[3] C.P. Silva, G.T.M. Silva, T. Costa, V.M.T. Carneiro, F. Siddique, A.J.A. Aquino, A.A. Freitas, J.A. Clark, E.M. Espinoza, V.I. Vullev, F.H. Quina, Pure Appl. Chem. 92 (2020) 255–263.
[4] X. Chen, T. Pradhan, F. Wang, J.S. Kim, J. Yoon, Chem. Rev. 112 (2012) 1910.
[5] Y.-H. Ahn, J.-S. Lee, Y.-T. Chang, J. Am. Chem. Soc. 129 (2007) 4510.
[6] Y.K. Kim, J.-S. Lee, X. Bi, H.-H. Ha, S.H. Ng, Y.-H. Ahn, J.-J. Lee, B.K. Wagner, P.A. Clemons, Y.-T. Chang, Angew. Chem. Int. Ed. 50 (2011) 2761.
[7] Y.K. Kim, H.-H. Ha, J.-S. Lee, X. Bi, Y.-H. Ahn, S. Hajar, J.-J. Lee, Y.-T. Chang, J. Am. Chem. Soc. 132 (2010) 576.
[8] L. Wu, K. Burgess, J. Org. Chem. 73 (2008) 8711.
[9] J.W. Han, J.C. Castro, K. Burgess, Tetrahedron Lett. 44 (2003) 9359.
[10] L. Yang, J.-Y. Niu, R. Sun, Y.-J. Xu, J.-F. Ge, Analyst 143 (2018) 1813–1819.
[11] L. Wang, W. Du, Z. Hu, K. Uvdal, L. Li, W. Huang, Angew. Chem. Int. Ed. 58 (2019) 14026–14043.
[12] J.R. Mann, M.K. Gannon, T.C. Fitzgibbons, M.R. Detty, D.F. Watson, J. Phys. Chem. C 112 (2008) 13057–13061.
[13] K.R. Mulhern, A. Orchard, D.F. Watson, M.R. Detty, Langmuir 28 (2012) 7071–7082.
[14] Z. Piontkowski, D.W. McCamant, J. Am. Chem. Soc. 140 (2018) 11046–11057.
[15] J.A. Tan, J.T. Rose, J.P. Cassidy, S.K. Rohatgi, K.L. Wustholz, J. Phys. Chem. C 120 (2016) 20710–20720.
[16] Z. Piontkowski, Y.-C. Wang, Y.-X. Liu, Y. Zhao, D.W.J. McCamant, Phys. Chem. C 124 (2020) 2851–2863.
[17] R.P. Sabatini, W.T. Eckenhoff, A. Orchard, K.R. Liwosz, M.R. Detty, D.F. Watson, D.W. McCamant, R. Eisenberg, J. Am. Chem. Soc. 136 (2014) 7740–7750.
[18] G. Li, M.F. Mark, H. Lv, D.W. McCamant, R. Eisenberg, J. Am. Chem. Soc. 140 (2018) 2575–2586.
[19] T. Erabi, M. Asahara, M. Miyamoto, K. Goto, M. Wada, Bull. Chem. Soc. Jpn. 75 (2002) 1325–1332.
[20] M.R. Valentino, M.K. Boyd, J. Org. Chem. 58 (1993) 5826–5831.
[21] G.-B. Shen, K. Xia, X.-T. Li, J.-L. Li, Y.-H. Fu, L. Yuan, X.-Q. Zhu, J. Phys. Chem. A 120 (2016) 1779–1799.
[22] M. Hagel, J. Liu, O. Muth, H.J.E. Rivera, E. Schwake, L. Sripanom, G. Henkel, G. Dyker, Eur. J. Org. Chem. (2007) 3573–3582.
[23] Y. Lu, F. Qu, B. Moore, D. Endicott, W. Kuester, J. Org. Chem. 73 (2008) 4763–4770.
[24] N.C. Deno, E. Sacher, J. Am. Chem. Soc. 87 (1965) 5120–5123.
[25] C.L. Dorsey, F.P. Gabbai, Main Group Chem. 9 (2010) 77–85.
[26] S.A. Ross, M. Pitie, B. Meunier, J. Chem Soc., Perkin Trans. 1 (2000) 571–574.
[27] F. Pina, M.J. Melo, C.A.T. Laia, A.J. Parola, J.C. Lima, Chem. Soc. Rev. 41 (2012) 869–908.
[28] E.E. Prust, E.J. Carlson, B.J. Dahl, Tetrahedron Lett. 53 (2012) 6433–6435.
[29] H. Decker, H. Felser, Ber. Dtsch. Chem. Ges. 41 (1909) 3755–3757.
[30] C.C. Barker, J. Chem. Soc. C (1969) 361–362.
[31] G.W.K. Cavill, F.M. Dean, J.F.E. Keenan, A. McGookin, A. Robertson, G.B. Smith, J. Chem. Soc. (1958) 1544–1549.
[32] Y. Yamaguchi, Y. Matsubara, T. Ochi, T. Wakamiya, Z.-I. Yoshida, J. Am. Chem. Soc. 130 (2008) 13867–13869.
[33] S. Kim, A. Oehlhof, B. Beile, H. Meier, Helv. Chim. Acta 92 (2009) 1023–1033.

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[34] H. Meier, Angew. Chem. Int. Ed. 44 (2005) 2482–2506.
[35] Y. Nagao, Y. Abe, T. Oyama, Y. Abe, T. Misono, Nippon Kagaku Kaishi 10 (1987) 1839–1845.
[36] E.M. Arnett, R.A. Flowers, , II, A.E. Meekhof, L. Miller, J. Am. Chem. Soc. 115 (1993) 12603–12604.
[37] D.H. Lee, M.J. Lee, H.M. Song, B.J. Song, K.D. Seo, M. Pastore, C. Anselmi, S. Fantacci, F. De Angelis, M.K. Nazeeruddin, M. Graetzel, H.K. Kim, Dyes Pigments 91 (2011) 192–198.
[38] Y. Ding, L. Mao, D. Xu, H. Xie, L. Yang, H. Xu, W. Geng, Y. Gao, C. Xia, X. Zhang, Q. Meng, D. Wu, J. Zhao, W. Hu, Bioorg. Med. Chem. Lett. 25 (2015) 2744–2748.
[39] D. Oesch, N.W. Luedtke, Chem. Commun. 51 (2015) 12641–12644.
[40] Z. Chen, X.-K. Liu, C.-J. Zheng, J. Ye, C.-L. Liu, F. Li, X.-M. Ou, C.-S. Lee, X.-H. Zhang, Chem. Mater. 27 (2015) 5206–5211.

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