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Modular assembly of azo photo-switches using click chemistry allows for predictable photo-behaviour

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ABSTRACT

Many azobenzene-based applications rely on variations in the 'head' group of the chromophores. We present a method to chemically modify azobenzenes quickly and easily, and report the effects that these modifications have on the properties of the azobenzene chromophores. Using now common 'click' chemistry, we have developed a methodology which can be applied in a one-pot fashion to rapidly vary the molecular structure, permitting the synthesis of libraries of dyes while allowing for the retention of photophysical characteristics. We validate this synthetic approach as not changing the nature of the chromophores in our testing of 17 derivatives, indicating that this is a good strategy for easy and rapid molecular tailoring. The results of this study will facilitate the use of these versatile molecules in material science, as it renders diverse structures attainable within one day instead of standard, multi-day syntheses per chromophore.

1. Introduction

Azobenzenes have become a favourite photoswitch to effect molecular and macromolecular change [1,2]. Azobenzene's microsecond timescale switching and high resistance to photobleaching – between 10^5 and 10^6 switches before fatigue [3] – are two of the superior properties which have led to its increasing use. These advantages have enabled azobenzene to make a large impact in vastly different fields from biological signalling [4–8], and control of peptide and protein structure [9–11], to photo-mechanical material changes [12–16], where the ultimate function is derived from functionalization at the end(s) of the azobenzene.

The variety of possible synthetic routes to produce azobenzene [17,18] allows for easy tuning of the chromophore absorbance which triggers isomerization from the stable *trans* state to the metastable *cis* state. Molecular substitution, for example with *ortho*-methoxy [19] or fluoro [20] groups, allows for easy activation of these chromophores with visible light coupled with long *cis* half-lives. Many fields of Science and Engineering are interested in azo switches, and the applications demonstrated at this point – such as controlling biological signalling and function – can no longer be met with off-the-shelf commercial dyes and require substantial synthetic undertakings, as the applications require different functionalities, or 'head' groups, appended to the azobenzene core and often large families of head groups for screening. These designer target structures can be met by synthetically experienced groups, but their complexity is hampering developments in less synthetically oriented fields. To enable researchers in all fields a more even footing in developing novel chromophores and architectures, completely new reactions and approaches are required which remove the need for specialized glassware, synthetic expertise, and inert conditions, and enormous preparation times, currently from days to many months.

We present here our approach to quickly and easily modify azobenzene chromophores in a single step while fulfilling these criteria, allowing new architectures from shelf-stable reagents using pre-determined facile reaction conditions on the hours timescale which can be applied in a one-pot fashion. The now ubiquitous 'click' chemistry is a facile method to vastly diversify the chemical structure of these azo-chromophores, and importantly retains the photophysical characteristics of the dye constant. This strategy allows for a 'bottom-up' approach where an alkyne-functionalized azo 'body' can be attached to a 'foot' such as a polymeric tail and using 'click' chemistry can be tailored with the

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desired 'head' group to impart specific form or function. This is in contrast to the 'top-down' approach which often requires different conditions for each functional chromophore.

There are several reactions that fall into the 'click' category–fast, high-yielding, regiospecific, and tolerant of functional groups. Among these are thiol-ene reactions [21], Diels–Alder cycloadditions [22], and copper-catalyzed alkyne-azide cycloadditions (CuAAC) [23–26]. Azobenzenes with 'clickable' functionalities have been used in various previous molecular and material applications [27–31]. However, not all of these applications employ 'click' functionality directly pendant to the azobenzene, and none investigate the effect of different 'head' groups to on photophysical changes to the chromophore. Given the ease with which organic azides can be synthesized opens up a vast library of interesting structures for study [32]. Added advantages of using 'click' chemistry are its compatibility with most functional groups [33] and easy application to polymers and films [24].

With the goal of preparing shelf-stable, highly functionalized small molecules and polymers with rigid linkers, the logical choice was to employ CuAAC with an alkyne functionality placed on the azobenzene. Organic azides can either be generated *in situ* or safely handled in small amounts [32,34] as they can be rapidly synthesized as needed to couple to the prepared alkynyl-azobenzene. A comparable method reported by the Feringa group employs a Staudinger–Bertozzi ligation, however our design doesn't require a bulky diphenyl phosphine bound to the azobenzene and benefits from faster reaction kinetics [35]. To keep these syntheses as efficient and facile as possible, all reactions except for Sonogashira couplings were conducted under atmospheric conditions at room temperature. We selected a 2:1 tetrahydrofuran:water blend with copper sulfate and sodium ascorbate as these conditions provided mild reaction and easy workup conditions [17,23,24].

2. Materials and methods

2.1. Material synthesis

Full synthetic details can be found in the Electronic Supplementary Information File. With the goal of keeping these syntheses as facile as possible, using the mildest conditions allowable, all reactions except for Sonogashira couplings (dry solvent, nitrogen atmosphere) were conducted under atmospheric conditions at room temperature. ^{1}H NMR spectra were acquired at 300 K, on a Varian-Mercury 300 MHz or 400 MHz spectrometer while ^{13}C NMR were acquired on a Varian-Mercury 300 MHz NMR. Chemical shifts are reported in ppm on the δ-scale using either the solvent signal for reference or internal TMS standard. High resolution mass spectrometry (HR-MS) was acquired on a Thermo Scientific Exactive Plus Orbitrap. Samples were ionized using either atmospheric-pressure chemical ionization (APCI) or electrospray ionization (ESI). All observed ions in positive and negative ionization modes are reported.

Trimethylsilylacetylene was obtained from Oakwood Chemicals (West Columbia, SC, USA), while N-(2-bromoethyl)phthalimide, (2-bromoethyl)benzene, (2-bromoethyl)cyclohexane, 1-bromobutane, 2-bromoethylphosphonate, and 4-bromo-2,2-diphenylbutyronitrile were obtained from Alfa Aesar (Ward Hill, MA, USA). All other chemicals were obtained from Sigma–Aldrich corporation (St. Louis, MO, USA).

All clicked N,N-diethylaniline model compounds (**4**–**20**) were synthesized in the same fashion. In a 50 mL round-bottom flask equipped with a stir bar, 50 mg N,N-diethyl-4-((4-ethynylphenyl)diazenyl)aniline (180 μmol, 1 equiv.), 720 μL 1 M CuSO4 (36 μmol, 0.2 equiv.) and 14 mg sodium ascorbate (72 μmol, 0.4 equiv.) were dissolved in 15 mL 2:1 THF:water. An excess of azide was added (540 μmol, 3 equiv.) and the solution was left to stir for two days to ensure complete reaction. Unless otherwise specified, the THF was removed under reduced pressure and the aqueous phase was extracted with 40 mL ethyl acetate. The organic phase was washed twice with 40 mL water then once with 40 mL brine, dried with MgSO4, and filtered. When needed, the crude products were purified using silica gel chromatography with ethyl acetate and hexane in a 0–40% gradient.

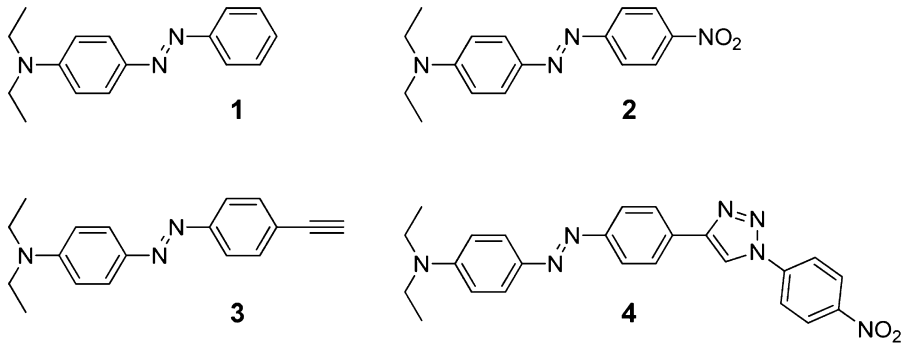
2.2. Optical characterization

Optical characterization was performed in dry spectral grade tetrahydrofuran (THF) on a Cary Bio 300 UV/vis for all compounds to measure the $\lambda_{max.}$ For Compounds **1** and **3**–**16**, the $t_{½}$ was also measured by tracking the time-dependant rise in absorption of the λ_{max} for 240 min following irradiation with a full spectrum white bulb for 10 s at 224 mW/cm^2. For Compound **2** due to its much faster decay kinetics, a pump-probe laser setup, using a Melles Griot Series 43 argon-ion laser was employed. The pump beam was typically in the range of 50 mW with a pump cycle of between 5 and 10 s to induce isomerization and ensure sample saturation back to the *trans* state. The pump irradiation time (~100–200 ms) was fast enough to avoid heating the sample, so the kinetic measurements can be considered to have been acquired at room temperature [36]. The probe beam was chopped mechanically at 1410 Hz, attenuated to between 8 and 120 μW (as needed) and passed through the sample into a photodiode detector, where the intensity was recorded as a function of time.

Extinction coefficients were measured by diluting a known amount of each chromophore in spectral grade THF in several concentrations and taking an average to minimize measurement error. The extent of isomerization was determined by irradiating THF solutions of each azobenzene derivative with a 405 nm diode laser widened through a lens to a power of 6 mW/cm^2 for 1 min. Further irradiation was demonstrated to provide no greater conversion to the *cis* form and this wavelength was more successful in inducing isomerization than white light or other wavelengths. The *cis* conversion was calculated by taking the absorbance value at the *trans* λ_{max} in the *cis* photostationary state and dividing by the all *trans* absorbance value. This gives a maximum *trans* content in solution. The minimum *cis* content is then that value subtracted from 1, and is considered the minimum value since the *trans* absorbance is lower but some of the absorbance at this wavelength comes as contributions from the n→π* transition and the cis π→π* transition. These could only be fully deconvoluted by achieving a 100% *cis* sample which is not possible in solution for these species.

3. Results and discussion

Our first concern in exploring molecular variation with this approach was whether the addition of different 'head' groups would affect the desired photophysical character of the azobenzene, such as accelerating thermal reconversion of the *trans* to *cis* state and red-shifting the absorption [3,37]. The structures in our first study (Scheme 1) compared the coupling of an electron-withdrawing nitrobenzene (**4**) on a simple dye (**3**) with a disperse red 1 analogue (**2**) and an aminoazobenzene (**1**) to determine the effects of substitution. As seen in Fig. 1, the expected slight red-shift in the λ_{max} upon derivatization of **3** from **1** results from the alkyne group, which is mildly electron-withdrawing and contributes to a slightly extended π conjugation system [38,39]. The CuAAC reaction of the alkyne results in a non-conjugated aromatic junction, electronically separating the two halves of the chromophores. This feature insulates the absorbance characteristics of the azobenzene from the added 'head' group, even in the case of



Scheme 1. Structures used to validate the 'click' approach to diversify azobenzenes. A model diethylaniline dye (**1**), a diethylaniline disperse red 1 dye (**2**), the 'clickable' diethylaniline derivative (**3**), and a 'clicked' nitrobenzene product (**4**).

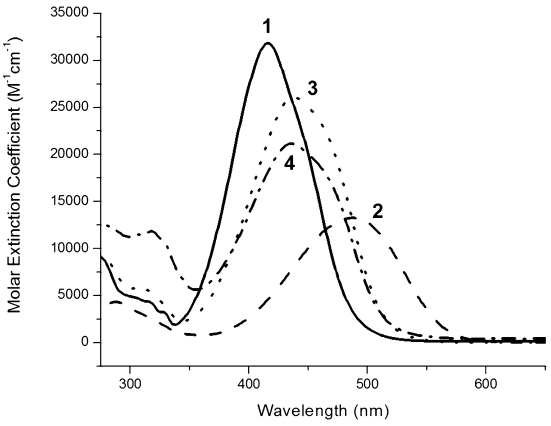


Fig. 1. UV–vis traces of Compounds **1**–**4** absorbance in THF.

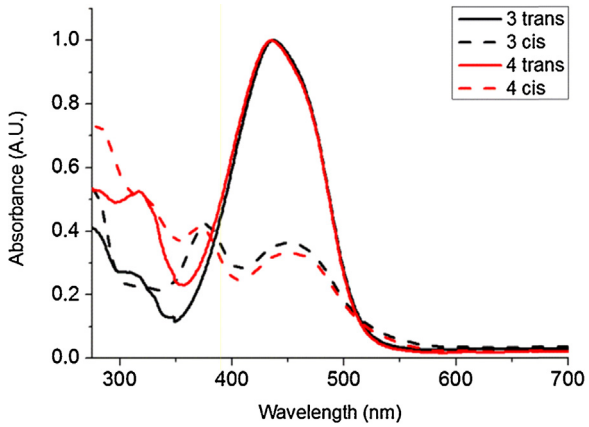


Fig. 2. Normalized UV–vis traces of Compounds **3** and **4** in the *trans* and *cis*-photostationary states, demonstrating near-identical absorbances at the pi–pi* azo transitions in the visible region >400 nm, but different absorbances in the UV due to the presence of the nitrobenzene moiety clicked on.

a powerfully electron-withdrawing group, which is why the sharp redshift observed between **1** and **2** is not repeated between **3** and **4**. This demonstrates the 'clicked' product retains the same $\pi \rightarrow \pi^*$ transition as the parent azobenzene, suggesting that derivatization is possible without changing the absorption character of the dyes, while retaining the molecular properties of the 'head'.

As important as the isomerization wavelength is the half-life of the chromophore: the desired application may require half-lives on the order of microseconds to hours [3]. As seen in Table 1, the conversion of **3** into **4** results in a slightly shorter half-life, however, nowhere near the three orders of magnitude difference in half-life observed between **1** over **2**. This provides a new route to generating azo dyes with specifically tailored structure, while retaining the half-life to which the chromophore was originally tuned. As can be seen in Fig. 2, the absorbance of chromophore **3** and **4** are very similar in the pi–pi* absorbance regions in both the *cis* and *trans* states, and maintain similar isosbestic points.

Since the addition of a highly electron-withdrawing group had little effect on the photophysical character of the dye, our next step was to validate different molecular structures to demonstrate the wide applicability of the technique. We selected a representative family of 17 aromatic and non-aromatic ionizable groups, alkyl chains, ethers, phosphonates and larger hydrophobic groups to test the limits of the technique, the structures of which are shown in Scheme 2.

The photophysical characteristics of these 17 derivatives are summarized in Table 2. The *trans*-state $\pi \rightarrow \pi^*$ transition of these chromophores causes an absorbance that fall within an essentially identical range of 432 ± 3 nm. Our method allows all of these diversified dyes to be actuated by the same light source. Critically, these 17 derivatives could be prepared in several days with relative ease, in contrast to classical synthetic methods which would require day to multi-day syntheses for each individual chromophore with

Table 1
λ_{max} and $t_{½}$ for Compounds **1**–**4** in THF.

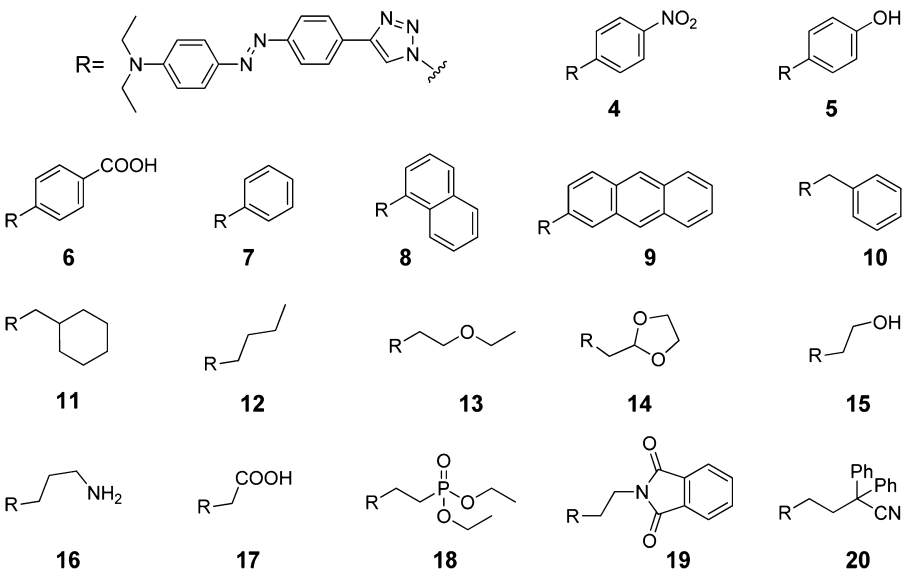
Compound	λ_{max} (nm)	$t_{½}$ [a]
1	417	265 ± 20 min
2	489	1.0 ± 0.1 s
3	436	59 ± 12 min
4	433	48 ± 12 min

[a] All kinetic runs are averages of 5 trials.

Table 2
λ_{max} and $t_{½}$ for Compounds **4**–**20** in THF.

Compound	λ_{max} (nm)	$t_{½}$ (min)[a]
4	433	48 ± 12
5	434	81 ± 11
6	435	69 ± 10
7	434	88 ± 4
8	432	26 ± 6
9	434	40 ± 20
10	432	84 ± 10
11	431	95 ± 2
12	431	75 ± 3
13	431	87 ± 1
14	433	90 ± 4
15	430	79 ± 3
16	430	59 ± 13
17	426	9 ± 1
18	431	50 ± 5
19	429	84 ± 3
20	431	52 ± 13

[a] All kinetic runs are averages of 5 trials.



Scheme 2. Family of 'heads' clicked: molecular architectures explored in this study, spanning a range of benzene derivatives, groups with ionizable functionalities, as well as aliphatic, and biologically exotic bulky substituents.

highly varied reaction conditions. As can be seen in the experimental section, all syntheses were standardized from azide preparation to final azo products.

The half-life decay of the functionalized groups shows a wider relative range than the absorbance. The half-lives for these dyes is measured by tracking the time-dependant rise in absorption of the $\pi \rightarrow \pi^*$ absorbance of the *trans* state and spans 9–90 min. Given that azobenzene dyes are known to have half-lives that can span eight orders of magnitude, retaining these derivatives to a single order of magnitude is significant and sufficient. There appears to be no obvious trend in the data obtained for this series. Chromophores with more electron-withdrawing groups which should provide faster isomerization (**4**,**6**) are only mildly faster than groups with moderate (**5**) or no electron donating ability (**7**). Increases in the size of **7** to

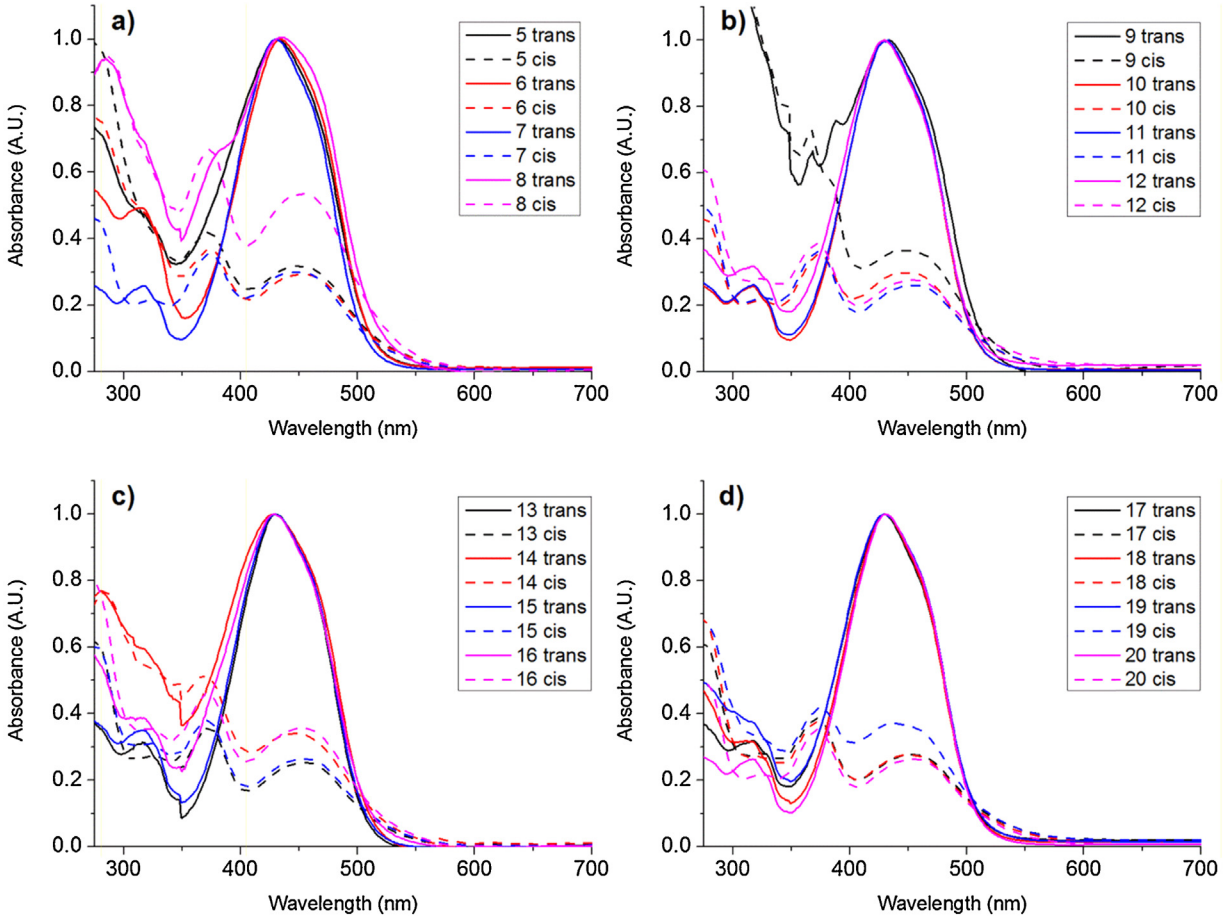


Fig. 3. Normalized UV–vis traces of compounds in the *trans* and *cis* states in THF solution, (a) **5**–**8**, (b) **9**–**12**, (c) **13**–**16**, and (d) **17**–**20**.

naphthyl (**8**) or anthracyl (**9**), shows more rapid isomerization, this may be due to steric bulk present in the *cis* state rendering it higher energy, which accelerates the isomerization to trans. The methylene group with a larger pendant arm, as in the benzyl (**10**) and cyclohexyl (**11**) derivatives, provides half-lives comparable to the basic phenyl (**7**), suggesting that added flexibility does not affect isomerization half-life. The abnormally fast half-life observed in **12** may be due to acid-catalyzed isomerization through protonation of the azo bond [40]. The N-phthalimide (**19**) functionality falls around the same value as the phenyl (**7**) while the far bulkier cyano diphenyl (**20**) is more in line with the anthracyl (**9**) derivative which further suggests molecular size does accelerate the thermal half-life.

For many applications, the exact value of the half-life is not as important as the magnitude, as such this 'click' approach can be a valuable tool in designing stimuli-responsive systems whose range in thermal reconversions kinetics are limited to one order of magnitude. The minimum extent of isomerization in the photostationary state with the exception of Compound **8** remains higher than 55% *cis* as determined by UV/vis spectroscopy (Fig. 3a–d). Given that this diethylaniline system has not been optimized to separate the *trans* and *cis* absorbances which would lead to higher isomerization ratios, this demonstrates that use of this technique would retain the high *cis* conversion that can be expected from classical azo chromophores. Additional to the benefits of this technique, the entire reaction scheme can be prepared rapidly within one-hour in a one-pot technique [41–43] yielding >70% product, or complete product conversion within 3 h when conducted at reflux (Supplementary Information).

4. Conclusions

We have designed, tested, and validated a new approach to functionalize azobenzene chromophores using 'click' chemistry with substantial advantages in cost, time, and ease. This approach allows for the molecular variation of the dyes, while retaining common photophysical characteristics, such as absorbance and half-life of the *cis-trans* isomerization, with a wide tolerance of functional groups. Furthermore, these modifications are easily achieved under ambient conditions from shelf-stable alkyne-functionalized azobenzene with relatively simple workup procedures. This approach can be used to easily construct azo dyes of new shapes as well as applications in larger molecular architectures. The ease and versatility of these syntheses opens the door to adoption by labs with less synthetic background in a one-pot fashion rapidly providing new dyes allowing dozens to be synthesized per day.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2014.07.013.

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