

## **A study of diazonium couplings with aromatic nucleophiles both in solution and on a polymer surface.**

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**Abstract:** Diazonium coupling is a technique finding wider application to materials and biological science, for hybridization and linking processes, and for the construction of responsive surface functionality. For this reason, detailed examination of solution and surface processes was warranted, and results of such a study are reported here. The modification of polystyrene surfaces was examined as a model, and the process compared to a solution mimic using *N,N*-dimethylaniline. It was confirmed that solution and solid surface reactions proceed in a similar manner in terms of the chemical functionality generated, but with lower chemical efficiency and reaction times slower for the latter, in a reaction which was pH dependent. The solution process was shown to give only the *trans*-azo *para*-coupled products. Whilst there are clear similarities between the solution and surface chemistry, the efficiency of coupling at a surface is not necessarily replicated in the chemical yield of the mimicking solution processes, but nonetheless provides an alternative to other Click-type surface modifications. It should not be assumed that such couplings occur with quantitative efficiency at the surface.

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## **Introduction**

The introduction of chromophoric groups onto polymers and biomaterials has been developed[1-3] and the azo-function ( $R-N=N-R'$ ) has become important in that regard,[4, 5] principally as a result of its ease of introduction and intense colour.[6] Because of the ease of formation of the azo-function, especially from aryl diazonium salts, it has also been used as a linking group[7] to couple polymers,[8] biomacromolecules and nanoparticles to surfaces[4], to introduce light switching,[9, 10] mechanical motion[11] and nanoelectronic properties,[12, 13] and for the control of wettability and swelling behaviour.[14-17] Moreover, photomediated *trans*- to *cis*- interconversion of the azo group is well known[18, 19] and has been used in the development in a wealth of photo-responsive materials, including reversible gel-sol systems,[20] polymers,[19, 21] molecular switches,[22, 23] and modified proteins.[24-27] Our interest in this area has been the use of the azo-link, formed by diazonium coupling with an activated nucleophilic surface,[28-31] as a key coupling component to give modified materials with new chemical surface functionality. While these materials may be characterised using combustion analysis, XPS analysis, IR and UV/visible spectroscopy, none of these techniques gives direct chemical evidence of the newly introduced azo-function, and of importance was whether the surface coupling reaction proceeds in a similar manner to its solution counterpart both in terms of (a) identity; and (b) efficiency of formation of the linking group. Therefore, we investigated coupling behaviour in solution using suitable model substrates and compared this to the modified surfaces in some detail, and report that work here.

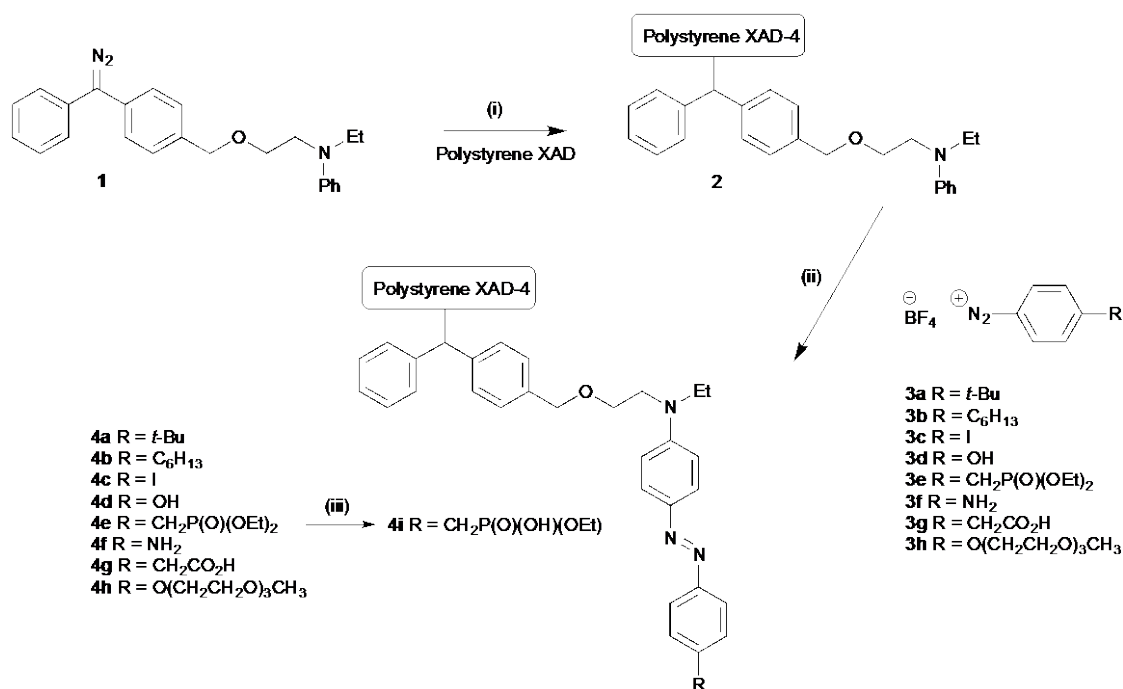
## Results and Discussion

### Polystyrene materials

Functional polystyrenes were prepared using our reported two-step modification process (Scheme 1).[32, 33] First, polystyrene (crosslinked, XAD-4) was reacted with an aniline-terminated carbene, by heating a solid dispersion of diaryl diazo-compound **1** on the polystyrene. The resulting modified polystyrene **2**, with a surface loading density of  $0.18\text{mmol g}^{-1}$  [32] and now activated to electrophilic substitution at the surface, was then further reacted with a range of diazonium salts **3a-h**, to give azo-functional polystyrenes **4a-h**. Alkaline hydrolysis of phosphate

diester **4d** gave phosphate monoester **4i**. Overall, this gave a range of surface-modified materials terminated with hexyl, hydroxyl, glycol, phosphonate diester, carboxylate and phosphonate functional groups.

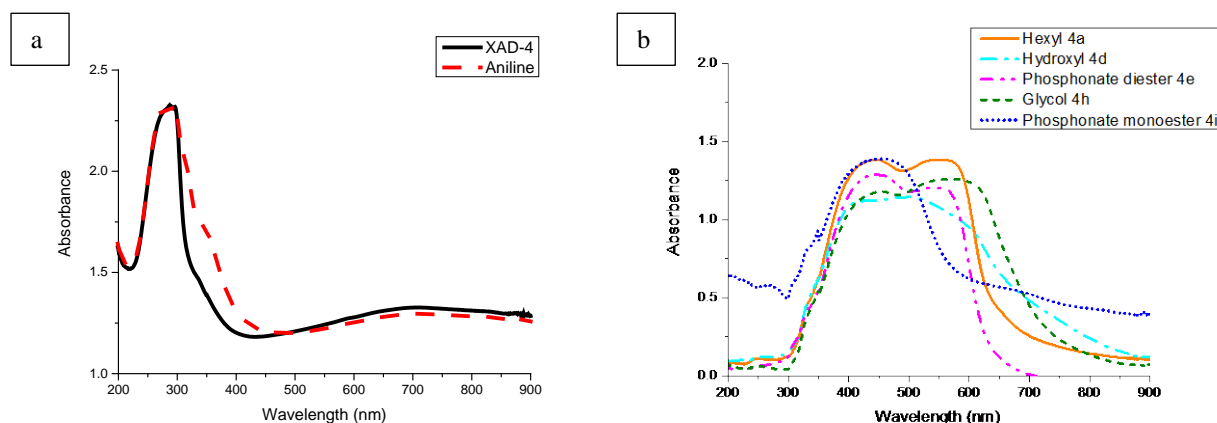
The UV-visible behaviour of azobenzene systems in solution has been investigated in detail; the wavelengths and intensity of the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  absorptions found to depend on whether azobenzene, aminoazobenzene, and pseudostilbene types are present.[34] *trans*-Azobenzene has two peaks of interest at 320 nm and 450 nm, ascribed to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the azo functionality, respectively.[18] The  $n \rightarrow \pi^*$  transition, however, is forbidden, so has a very small extinction coefficient, often resulting in the absence of its associated signal.[35] Since the coupling process in Scheme 1 involves an electron-donating amine component, a significant bathochromic shift in the  $\pi \rightarrow \pi^*$  transition was expected. Moreover, while the *trans*-azo geometry is the thermally stable one, the *cis*- form can be accessed by exposure to UV light, resulting in a change in the UV spectrum: the  $\pi \rightarrow \pi^*$  transition undergoes a hypsochromic shift to a lower wavelength (from ~320 to ~270 nm), but the  $n \rightarrow \pi^*$  increases by only a small amount.[17, 18, 36] However, while reports of UV analysis of azobenzene-modified materials are less common, and in any case have typically been achieved in solution,[17, 36] a solid cellulose surface-modified with azobenzene has been used to control wettability and exhibited similar trends to those observed in solution.[37]



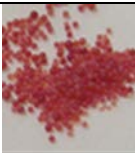
**Scheme 1: Preparation of polystyrene materials.** Conditions: (i) heat to 120 °C; (ii) diazonium salt solution in EtOH, 18 hrs, 0-5 °C; (iii) 5% aq. NaOH, 18 hrs.

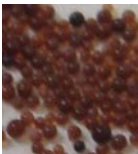
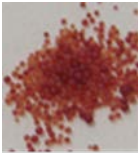
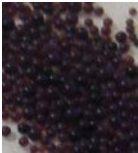

All of the materials **4a-i** are highly coloured (either red-orange or purple), with the exception of amine-terminated **4f** (yellow) (Table 1). Diffuse reflectance UV-Vis spectroscopic analysis of a selection of the materials showed a significant change in chromophore after surface modification (Figure 1 and Table 1). Figure 1a shows the UV absorbance spectra of the unmodified XAD-4 beads, as-received but after washing, along with the diazo modified aniline material **2**. Both materials exhibit peaks at 287 nm, as a result of the  $\pi \rightarrow \pi^*$  transition for the aromatic rings of the polystyrene substrate. Aniline **2**, however, additionally shows a broader absorbance along with a shoulder peak at 346 nm, resulting from a bathochromic shift due to the donation of the aniline N lone pair in the surface groups, and providing clear evidence for the surface modification. Figure 1b shows the background-adjusted UV spectra obtained from a selection of the coupled materials **4b, d, e, h, i**. This data clearly indicates that the surface modification has made a significant chromophoric change to the materials, with materials all having a broad absorbance at wavelengths in the range of 410-650 nm, consistent with their observed colour. Materials **4b, d, e** and **h** have two broad peaks, with a lower peak at 410-460 nm and a second peak at 497-576 nm. The first peak results from the  $\pi \rightarrow \pi^*$  transition of the azo bond, consistent with a *trans*-azo geometry.[37]

The second and higher wavelength peak is due to the protonation at either of the azo or amine sites, producing the azonium or ammonium salts, respectively.[38] An ammonium cation is known to exhibit a hypsochromic shift due to the loss of the electron-donating ability of the nitrogen lone-pair, while protonation at the azo site results in a significant bathochromic shift to the region of ~500 nm. Since the diazonium coupling reaction used for the polymer modification was conducted under acidic conditions, such protonation is plausible and to be expected. By contrast, phosphonate monoester terminated **4i** has only one peak at 453 nm; it was obtained by hydrolysis of **4e** in aqueous sodium hydroxide, and therefore the protonated form is not present; for this reason, the modified material is different in colour (yellow) compared to all of the other materials. This data all supports the identity of the newly introduced coupling group as being an azo- function.



**Figure 1:** UV spectra of (a) uncoupled polystyrene XAD-4 **1** and aniline **2**; and (b) coupled materials **4a, d, e, h**. Absorbance has been corrected using aniline terminated material **2** as a reference.

Material (R)	Appearance	Peak 1	Peak 2
		(nm) <i>Absorbance</i>	(nm) <i>Absorbance</i>
<b>4b</b> (C <sub>6</sub> H <sub>13</sub> )		446 <i>1.38</i>	540 <i>1.38</i>

<b>4d</b> (OH)		410 <i>1.11</i>	497 <i>1.14</i>
<b>4e</b> (CH <sub>2</sub> P(O)(OEt) <sub>2</sub> )		450 <i>1.29</i>	536 <i>1.20</i>
<b>4h</b> ((OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> )		455 <i>1.18</i>	576 <i>1.26</i>
<b>4i</b> (CH <sub>2</sub> P(O)(OEt)(OH))		453 <i>1.39</i>	-

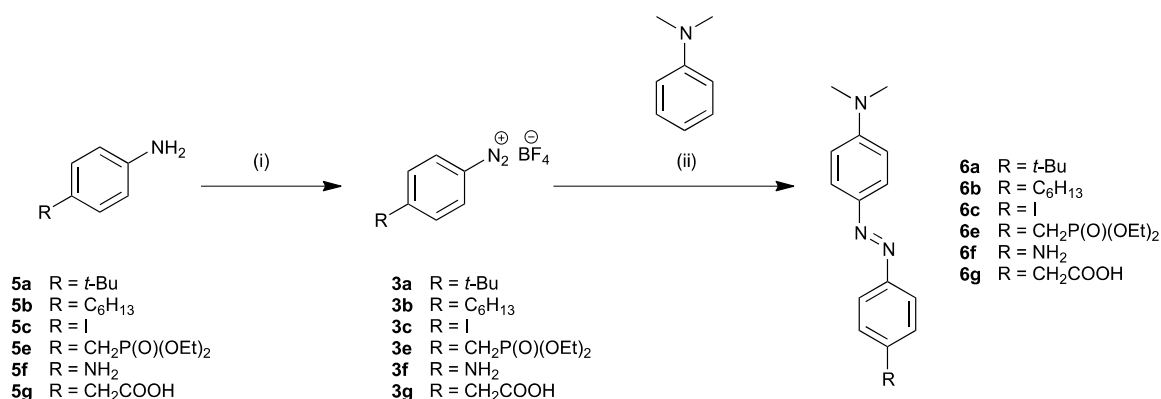
**Table 1:** Peaks observed by diffuse UV-Vis spectroscopic analysis of coupled materials. Absorbance has been corrected using aniline terminated material **2** as a reference. Photographs reproduced from Ref.[32] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

The efficiency of the coupling was estimated by comparison of surface loading of the modified polymers (as measured from nitrogen combustion data) relative to that of the starting material **2** (Table 2).[32] Coupling efficiency was typically in the range 28-67%; the value for iodo modified polymer **4c** was significantly higher than these, and this may be due to activation of the iodoaryl unit towards further diazonium coupling (see below).

### Solution Coupling Reactions

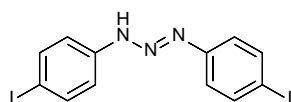
To further understand these surface reactions, a solution study was conducted using *N,N*-dimethylaniline as a model substrate, along with a similar selection of diazonium salts (Scheme 2). This allowed for spectroscopic confirmation of the identity of the coupling products in solution, which was otherwise not possible for the modified polystyrene materials. Since the effect of pH on the diazonium coupling reaction is known in solution,[39-41] it was similarly examined here. The diazonium salts were synthesised in ethanol at -5-0 °C using isopentyl nitrite, along with the relevant aniline **6a-f** and tetrafluoroboric acid (Scheme 2), using the literature approach.[42] The colourimetric H-acid test[43] was used to confirm the formation of the diazonium salts in step (i) of

Scheme 2. During the coupling reaction, a significant colour developed on addition of the reagents, which had stabilised by completion of reaction (typically 1h).



**Scheme 2: Solution diazonium coupling.** Conditions: i) isopentyl nitrite, HBF<sub>4</sub>, EtOH, -5 °C; ii) Procedure A: **3a-c**, **e-g** were added then the mixture warmed to room temperature and stirred; Procedure B: NaOAc then **3a-c**, **e-g** were added and the mixture stirred at room temperature.

The diazonium salts were reacted with *N,N*-dimethylaniline using two protocols. For the first (Method A), *N,N*-dimethylaniline was added directly and the mixture warmed to room temperature. For the second (Method B), sodium acetate was initially used to adjust the pH of the diazonium salt mixture, followed by the addition of dimethylaniline and warming to room temperature. The reactions were followed by TLC analysis; the reactions times were variable and complete consumption of *N,N*-dimethylaniline was rarely observed (Table 2). Unreacted amines **5a-c**, **5e-g** from the alkyl, acid, phosphonate diester and iodo cases were observed, although no unreacted *p*-phenylenediamine **5f** was recovered. In one case, 1,3-bis(4-iodophenyl)triaz-1-ene **7** was detected by mass spectrometric and NMR spectroscopic analysis of the crude mixture generated from Method B, as a result of the reaction of the diazonium salt **3c** with starting 4-iodoaniline **5c**. This product was not observed when the reaction was done in acidic medium (Method A). It is known that use of mildly basic conditions can also result in *N*-coupling when there are primary anilines present,[4] as there would be if unreacted 4-iodoaniline was present. The difference in the coupling yields are likely to result both from variation in the efficiency of the diazonium salt formation, and the diazonium coupling process itself.



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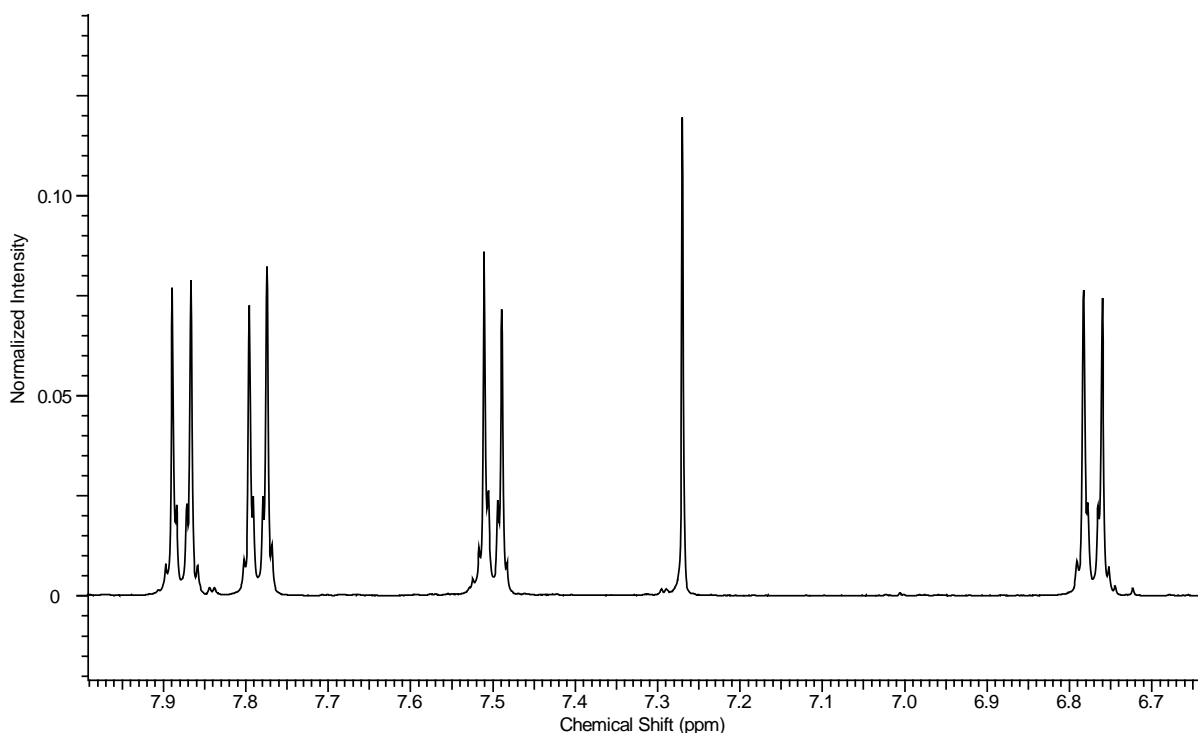
Product	R	Method A		Method B		Materials Surface Loading <sup>b</sup>		
		Reaction time (hr)	Yield (%)	Reaction time (hr)	Yield (%)	Polymer	mmol of surface modification /g of polymer	Coupling Efficiency(%)
<b>6a</b>	<i>t</i> -Bu	18	72	4	91	<b>4a</b>	0.062	34
<b>6b</b>	C <sub>6</sub> H <sub>13</sub>	18	20	20	73	<b>4b</b>	0.067	37
<b>6c</b>	I	0.5	64	0.5	57	<b>4c</b>	0.357	198
<b>6e</b>	CH <sub>2</sub> P(O)(OEt) <sub>2</sub>	1	96	1	46	<b>4e</b>	0.121	67
<b>6f</b>	NH <sub>2</sub>	18	0	18	12 <sup>a</sup>	<b>4f</b>	0.046	26
<b>6g</b>	CH <sub>2</sub> COOH	20	95	18	34	<b>4g</b>	0.052	28

**Table 2.** Results of solution diazonium coupling. a) Yield calculated from NMR data; b) Determined from combustion analysis of the analogous polystyrene based materials – see reference [32]. Coupling efficiency determined by comparison of surface loading relative to that of the starting material **2** (with a surface loading density of 0.18mmolg<sup>-1</sup>.[32]

The introduction of sodium acetate to control the pH of the reactions (Method B) gave mixed results; while yields of reactions for the hexyl **6b**, amine **6f** and *t*-butyl **6a** systems were increased under these conditions, the acid **6g**, phosphonate **6e** and iodo **6i** salts reactions proceeded with lower yields. It is notable that that the acid and amine system **6f** and **6g** were difficult to purify after reaction as a result of their polarity. Overall, these data point to increased reactivity with electron releasing groups (formation of **6a,b**) and lower reactivity with electron withdrawing groups (formation of **6c,e,g**). The case of **6f** is different, and suggests that reaction under acidic conditions is poor, and best achieved under basic conditions when the amine groups are not protonated. It is apparent that an efficient coupling in the solution phase (that is, high chemical yield) should not be assumed to imply an efficient material surface coupling (that is, high surface loading) and or efficient coupling (Table 2).



NMR spectroscopic analysis of all the products **6a-c**, **e-g** revealed that only the *para* coupled products were produced; there was no evidence of reaction at the *ortho* position. Thus, in the spectra for each product, four apparent doublets were observed in the range of 6.7-7.9 ppm, corresponding to the two *para*-substituted systems, exemplified for *t*-butyl **6a** (Figure 2). Furthermore, the symmetry of this NMR spectrum also confirms the formation of the *trans*-azo isomers, and there is no evidence for the *cis* form. These azobenzene compounds are significantly coloured in solution and absorb light strongly in the region 200-800 nm (Table 3). The electron-donating dimethyl amine group induces a significant bathochromic shift, compared to unsubstituted azobenzene, so that the  $\pi \rightarrow \pi^*$  azo transition ranges from 410 to 425 nm. Iodo-terminated **6c** has the largest shift as a result of the push-pull effect of the electron donating and withdrawing groups at either end of the molecule, and which increases the wavelength of adsorption.[38, 44] The weak  $n \rightarrow \pi^*$  transition was not observed, and in any case may be obscured by the broad peak of the  $\pi \rightarrow \pi^*$  azo transition. The compounds also absorbed at 250-285 nm, which is due to the  $\pi \rightarrow \pi^*$  benzene transition.



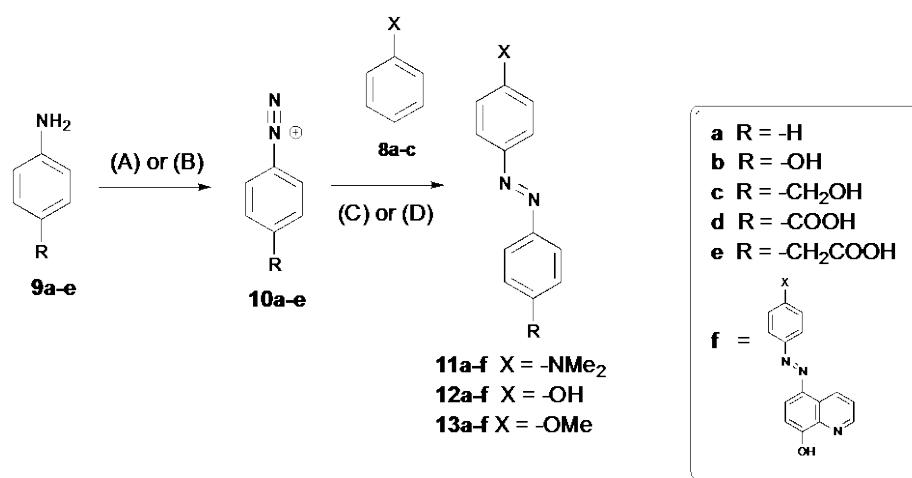
**Figure 2:** NMR Spectrum of the aromatic region for exemplified for *t*-butyl **6a**

Product	R	$\pi \rightarrow \pi^*$ benzene		$\pi \rightarrow \pi^*$ azobenzene	
		$\lambda_{\max}$ (nm)	Extinction coefficient (mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> )	$\lambda_{\max}$ (nm)	Extinction coefficient (mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> )
<b>6a</b>	t-Bu	285	3200	412	5040
<b>6b</b>	C <sub>6</sub> H <sub>13</sub>	255	11000	410	24000
<b>6c</b>	I	273	2400	425	3840
<b>6e</b>	CH <sub>2</sub> P(O)(OEt) <sub>2</sub>	263	10000	416	25000
<b>6f</b>	NH <sub>2</sub>	250	4700	413	5980
<b>6g</b>	CH <sub>2</sub> COOH	262	4800	415	8500

**Table 3:** UV-vis spectroscopic analysis of azo- coupled products **6**.

Of further interest was an assessment of this coupling reaction with a range of electron-rich substrates; benzenes **8a-c**, with NMe<sub>2</sub>, OMe and OH substitution respectively, were chosen. These were coupled with a diazonium salts **10a-e**, prepared from their respective amines **9a-e** using either of two conditions (Methods A or B, Scheme 3), and the outcomes are indicated in Table 3. Of interest was that the azo-coupling, at least for dimethylaniline, generally gave better yields with condition A, using NaNO<sub>2</sub> with HCl in THF and H<sub>2</sub>O, compared to condition B, using isopentyl nitrite with HBF<sub>4</sub> in EtOH, and this could be due to the counter-ion of the diazonium salt, since the non-nucleophilic tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) anion is known to enhance the stability of the diazonium salt compared to nucleophilic chloride (Cl<sup>-</sup>) anion.[45, 46] Importantly, the azo-coupling reactions were found to be pH dependent: thus, the addition of 1 equivalent of NaOAc to reduce the acidity of the reaction mixture to about pH 4 - 5 could result in 47 – 65 % increase in yields. An additional 1 equivalent of NaOAc also improved yields further by about 10 – 18%. It would appear that by

controlling the pH of the mixture to about pH 4 – 5, protonation of the substrate, which could inhibit the coupling reaction, is avoided.



**Scheme 2**

**Scheme 3. Azo coupling reactions.** Conditions: (A): NaNO<sub>2</sub>, HCl, THF, H<sub>2</sub>O; (B): Isopentyl nitrite, HBF<sub>4</sub>, EtOH; (C): without NaOAc; (D), with NaOAc.

By contrast, however, not all diazonium salts reacted cleanly with phenol or dimethylaniline to give the desired products. Complex mixtures resulted from the coupling with diazonium salts **10b,e**, and although it was not possible to purify and isolate the products **11b,e** and **12b,e**, these products were detected in the reaction mixtures with their molecular ion (as [M+H]<sup>+</sup> or [M-H]<sup>-</sup>) being the base peak. Importantly, there was little or no reaction of the diazonium salts with anisole (entries 29-34). This is consistent with reports that such neutral species are not sufficiently nucleophilic for the azo coupling reaction to take place,[4] and that a more electrophilic diazonium salt is required.[46-49] Overall, while diazonium couplings with good efficiency may be expected for phenol and dimethylaniline systems, but less so for anisole type systems, in solution, the latter on a modified surface show much better reactivity.[30, 50]

Entry	X	R	Product	Conditions	Yield / %
1	-NMe <sub>2</sub>	-H	<b>11a</b>	(A) + (C)	40
2	-NMe <sub>2</sub>	-H	<b>11a</b>	(A) + (D) <sup>a</sup>	98
3	-NMe <sub>2</sub>	-H	<b>11a</b>	(B) + (C)	20
4	-NMe <sub>2</sub>	-H	<b>11a</b>	(B) + (D) <sup>a</sup>	67
5	-NMe <sub>2</sub>	-OH	<b>11b</b>	(A) + (D) <sup>a</sup>	Complex mixture <sup>c</sup>
6	-NMe <sub>2</sub>	-CH <sub>2</sub> OH	<b>11c</b>	(A) + (D) <sup>a</sup>	96
7	-NMe <sub>2</sub>	-COOH	<b>11d</b>	(A) + (D) <sup>a</sup>	97
8	-NMe <sub>2</sub>	-CH <sub>2</sub> COOH	<b>11e</b>	(A) + (C)	Complex mixture <sup>c</sup>
9	-NMe <sub>2</sub>	-CH <sub>2</sub> COOH	<b>11e</b>	(A) + (D) <sup>a</sup>	Complex mixture <sup>c</sup>

<b>10</b>	-NMe <sub>2</sub>	-8-hydroxyquinoline	<b>11f</b>	(A)	Complex mixture
<b>11</b>	-NMe <sub>2</sub>	-8-hydroxyquinoline	<b>11f</b>	(A) + (D) <sup>a</sup>	Complex mixture
<b>12</b>	-OH	-H	<b>12a</b>	(A) + (C)	34
<b>13</b>	-OH	-H	<b>12a</b>	(A) + (D) <sup>a</sup>	82
<b>14</b>	-OH	-H	<b>12a</b>	(A) + (D) <sup>b</sup>	95
<b>15</b>	-OH	-OH	<b>12b</b>	(A) + (C)	Complex mixture <sup>c</sup>
<b>16</b>	-OH	-OH	<b>12b</b>	(A) + (D) <sup>a</sup>	Complex mixture <sup>c</sup>
<b>17</b>	-OH	-CH <sub>2</sub> OH	<b>12c</b>	(A) + (C)	12
<b>18</b>	-OH	-CH <sub>2</sub> OH	<b>12c</b>	(A) + (D) <sup>a</sup>	77
<b>19</b>	-OH	-CH <sub>2</sub> OH	<b>12c</b>	(A) + (D) <sup>b</sup>	87
<b>20</b>	-OH	-COOH	<b>12d</b>	(A)	Impure
<b>21</b>	-OH	-COOH	<b>12d</b>	(A) + (D) <sup>a</sup>	70
<b>22</b>	-OH	-COOH	<b>12d</b>	(A) + (D) <sup>b</sup>	88
<b>23</b>	-OH	-CH <sub>2</sub> COOH	<b>12e</b>	(A) + (C)	Complex mixture <sup>c</sup>
<b>24</b>	-OH	-CH <sub>2</sub> COOH	<b>12e</b>	(A) + (D) <sup>a</sup>	Complex mixture <sup>c</sup>
<b>25</b>	-OH	-CH <sub>2</sub> COOH	<b>12e</b>	(A) + (D) <sup>b</sup>	Complex mixture <sup>c</sup>
<b>26</b>	-OH	-8-hydroxyquinoline	<b>12f</b>	(A)	Complex mixture
<b>27</b>	-OH	-8-hydroxyquinoline	<b>12f</b>	(A) + (D) <sup>a</sup>	Complex mixture
<b>28</b>	-OH	-8-hydroxyquinoline	<b>12f</b>	(A) + (D) <sup>b</sup>	Complex mixture
<b>29</b>	-OMe	-H	<b>13a</b>	(A) + (D) <sup>b</sup>	No reaction
<b>30</b>	-OMe	-OH	<b>13b</b>	(A) + (D) <sup>b</sup>	No reaction
<b>31</b>	-OMe	-CH <sub>2</sub> OH	<b>13c</b>	(A) + (D) <sup>b</sup>	No reaction
<b>32</b>	-OMe	-COOH	<b>13d</b>	(A) + (D) <sup>b</sup>	No reaction
<b>33</b>	-OMe	-CH <sub>2</sub> COOH	<b>13e</b>	(A) + (D) <sup>b</sup>	No reaction
<b>34</b>	-OMe	-8-hydroxyquinoline	<b>13f</b>	(A) + (D) <sup>b</sup>	No reaction

<sup>a</sup> Using 1 equiv of NaOAc; <sup>b</sup> Using 2 equiv of NaOAc; <sup>c</sup> Mass spectrometry showed that [M+H]<sup>+</sup> or [M-H]<sup>-</sup> was base peak.

**Table 4.** Azo coupling reactions performed according to Scheme 3.

## Conclusions

An investigation of solution and solid-state azobenzene coupling processes using a combination of spectroscopic techniques has provided clear evidence of similar pathways for each, resulting from azo-group formation. The solid phase azo-coupling process can be slow and is pH dependent, and generates modified polymers in the protonated form unless the coupled product is subjected to a base wash. Evidence for *para*-coupling in solution was obtained, and with increased steric restraints on a surface, it is reasonable to expect that surface couplings are also *para* directed. Importantly, neither solution nor surface coupling is quantitative, and appropriate reaction time needs to be allowed to ensure high levels of conversion. From the similarities of the UV absorption data between solution and solid phase, there is clear evidence for azo-coupling at the electron-rich activated surface generated after carbene insertion as indicated in Scheme 1, but of interest is that

recent work has shown that diazonium coupling reactions with Carbon Black may proceed by loss of nitrogen followed by surface coupling in a radical mechanism;[51, 52] there is of course the possibility that some similar radical mediated coupling may occur in the system studied here-in. Such azo- couplings may be considered to be another example of “Click”-type chemical modification methodology, suitable for wide application and especially suitable for solid materials.[53]

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## **Experimental**

Reactions were carried out in oven-dried flasks open to the atmosphere using standard solvents, petrol refers to petroleum ether with boiling point 40-60 °C. Water refers to the use of de-ionised water. Where necessary, temperatures below room temperature were achieved using cooling baths; ice/NaCl/water (-5 °C), ice/water (0 °C) or by standing in the fridge in the case of polymer modification. When possible, reactions were followed with thin layer chromatography (TLC) with Merck aluminium foil backed sheets pre-coated with 0.2 mm Kieselgel 60 F<sub>254</sub> silica gel, product spots were visualised with UV fluorescence ( $\lambda_{\text{max}}$  254 nm). Column chromatography was performed with Merck Geduran Si 60 silica gel (0.040-0.063 mm). Solvents were evaporated under reduced pressure at 40 °C on a Buchi Rotavapor R-210 with a Vacuubrand CVC2 pump and pressure control system. Characterisation of compounds was done using the following equipment and settings. Melting points were measured with a Stuart Scientific SMP1 melting point apparatus. UV-visible spectra were obtained with a Perkin-Elmer UV Lamda 14P spectrometer with solutions

in DCM; the path length is 1 cm and the data is reported in nanometers (nm) with the molar extinction coefficients ( $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ). Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometers; selected absorption maxima are reported in wavenumbers ( $\text{cm}^{-1}$ ).  $^1\text{H}$  NMR were recorded on Bruker DPX200 (200 MHz), DPX400 (400 MHz), DQX400 (400 MHz) and AVC500 (500 MHz) spectrometers and COSY were obtained on a Bruker DQX400 and AVC500.  $^{13}\text{C}$  NMR were recorded on DQX400 (100 MHz) and AVC500 (125 MHz) spectrometers, HMBC, HSQC HMQC and DEPT spectra were obtained with these instruments also. Chemical shifts ( $\delta_{\text{H}}$ ,  $\delta_{\text{C}}$ ) are reported in parts per million (ppm), coupling constants ( $J$ ) are in hertz (Hz) and the following abbreviations are used: s (singlet), br s (broad singlet), d (doublet), dd (doublet doublet), t (triplet), q (quartet), m (multiplet), app. (apparent). Low resolution mass spectra ( $m/z$ ) were obtained with a Fisons Platform spectrometer with electrospray ionisation (ESI) and a Fisons AutoSpec-oaTpf spectrometer with field ionisation (FI). A Bruker microTOF was used to obtain high resolution mass spectra;  $m/z$  values are reported in Daltons and their intensities are a function of the base peak. Diffuse reflectance spectroscopy was performed using an Agilent Cary 4000 UV Vis spectrometer with a Pike Veemac Diffuse IR accessory. Combustion analysis was provided by MEDAC Ltd, Surrey, UK.

### **Polystyrene materials 4a-4i**

For extensive information concerning preparation and characterisation see our previously published work.[31, 32]

### **Solution Diazonium couplings**

#### **Procedure A: Procedure for diazonium coupling to *N,N*-dimethylaniline.**

A solution of the amine (1 eq) in EtOH was stirred at  $-5\text{ }^{\circ}\text{C}$ . Isopentyl nitrite (1 eq) and tetrafluoroboric acid (2 eq) were added and the mixture was stirred for 1 hour at  $-5\text{ }^{\circ}\text{C}$ . *N,N*-dimethylaniline (1 eq) was added and the mixture stirred at room temperature for the time period

given in Table 2. The EtOH was removed *in vacuo* then the residue dissolved in DCM and washed with sat. aq. K<sub>2</sub>CO<sub>3</sub>. The aqueous phase was washed with DCM until the resulting organic phase was colourless. The organic fractions were combined, dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. Purification by silica column chromatography was performed if necessary and the yields of the reactions are in Table 2.

**Procedure B: Diazonium coupling to *N,N*-dimethyl aniline with adjusted pH.**

A solution of the amine (1 eq) in EtOH was set to stir at -5 °C. Isopentyl nitrite (1 eq) and tetrafluoroboric acid (2 eq) were added and the mixture was stirred for 1 hour at -5 °C. Sodium acetate (1 eq) followed by *N,N*-dimethylaniline (1 eq) were added then the mixture stirred at room temperature for the time periods in Table 2. The EtOH was removed *in vacuo* then the residue dissolved in DCM and washed with water. The aqueous phase was washed with DCM until the resulting organic phase was colourless. All the organic fractions were combined, dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. Purification by silica column chromatography was performed if necessary and the yields are displayed in Table 2.

**(*E*)-4-((4'-(*tert*-Butyl)phenyl)diazenyl)-*N,N*-dimethylaniline 6a.**

Product **6a** was purified by column chromatography (eluent 20:1 petrol:EtOAc) and isolated as a red solid. *R*<sub>f</sub> 0.44, 15:1 (petrol:EtOAc); mp 156-158 °C (lit.[54] 137-137.5 °C); λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>)/nm 412 (5040 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); ν<sub>max</sub>(neat)/cm<sup>-1</sup> 2964 (C-H), 1600 (N=N), 1515, 1442, 1520, 1362 (C-N), 1229, 1159, 1140, 945, 839, 818; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 1.38 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.09 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 6.77 (2H, app. d *J* 9.2, H-2, 6), 7.51 (2H, app. d *J* 8.8, H-2', 6'), 7.79 (2H, app. d *J* 8.8, H-3', 5'), 7.88 (2H, app. d *J* 9.2, H-5, 3); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 31.4 (C(CH<sub>3</sub>)<sub>3</sub>), 34.8 (C(CH<sub>3</sub>)<sub>3</sub>), 40.3 (N(CH<sub>3</sub>)<sub>2</sub>), 111.5 (C-2, 6), 121.9 (C-3', 5'), 124.7 (C-3, 5), 125.8 (C-2', 6'), 143.8 (C-1), 151.1 (C-1'), 152.2 (C-4), 152.7 (C-4'); *m/z* (ESI<sup>+</sup>) 282 ([M+H]<sup>+</sup>, 100%); HRMS (ESI<sup>+</sup>) calculated for C<sub>18</sub>H<sub>24</sub>N<sub>3</sub> *m/z* [M+H]<sup>+</sup>: 282.1965; found, 282.1969.

**(*E*)-4-((4'-Hexylphenyl)diazenyl)-*N,N*-dimethylaniline 6b.**

Product **6b** was purified by silica column chromatography (eluent 20:1 petrol:EtOAc) and was isolated as an orange solid.  $R_f$  0.58 (10:1 petrol:EtOAc); m.p. 74 °C;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  410 (24000  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ );  $\nu_{\max}(\text{neat})/\text{cm}^{-1}$  2925 (C-H), 2854 (C-H), 1599 (N=N), 1515, 1443, 1400, 1393 (C-N), 1230, 1154, 1139, 946, 818;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.91-0.94 (3H, m,  $\text{CH}_3\text{C}_5\text{H}_{10}\text{Ar}$ ), 1.35 (6H, br s,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_2\text{H}_5\text{Ar}$ ), 1.64-1.72 (2H, m,  $\text{C}_4\text{H}_9\text{CH}_2\text{CH}_2\text{Ar}$ ), 2.96 (2H, t  $J$  7.7,  $\text{C}_5\text{H}_{11}\text{CH}_2\text{Ar}$ ), 3.08 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 6.78 (2H, app. d  $J$  9.1, H-2, 6), 7.32 (2H, app. d  $J$  8.3, H-2', 6'), 7.80 (2H, app. d  $J$  8.3, H-3', 5'), 7.90 (2H, app. d  $J$  9.1, H-3, 5);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 14.2 ( $\text{CH}_3\text{C}_5\text{H}_{10}\text{Ar}$ ), 22.6, 29.0, 31.4 and 31.7 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ar}$ ), 35.8 ( $\text{C}_5\text{H}_{11}\text{CH}_2$ ), 40.3 ( $\text{N}(\text{CH}_3)_2$ ), 111.5 (C-2, 6), 122.2 (C-3, 5), 124.8 (C-3', 5'), 129.0 (C-2', 6'), 143.8 (C-1), 144.7 (C-4'), 151.5 (C-1'), 152.2 (C-4); HRMS ( $\text{ESI}^+$ ) calculated for  $\text{C}_{20}\text{H}_{28}\text{N}_3$   $m/z$   $[\text{M}+\text{H}]^+$ : 309.2205; found, 309.2216.

**(*E*)-4-((4'-Iodophenyl)diazenyl)-*N,N*-dimethylaniline 6c.**

Product **6c** was purified with silica column chromatography (eluent 30:1 petrol:EtOAc) affording an orange solid.  $R_f$  0.67 (4:1 petrol:EtOAc); mp 166-169 °C, lit.[55] 163.5-164 °C;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  425 (3840  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ );  $\nu_{\max}(\text{neat})/\text{cm}^{-1}$  2922 (C-H), 1602, 1514, 1470, 1419, 1363 (C-N), 1231, 1156, 1051, 827, 733, 700, 649;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 3.10 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 6.76 (2H, app. d  $J$  9.2, H-2, 6), 7.59 (2H, app. d  $J$  8.6, H-2', 6'), 7.81 (2H, app. d  $J$  8.6, H-3', 5'), 7.88 (2H, app. d  $J$  9.2, H-3, 5);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 40.3 ( $\text{N}(\text{CH}_3)_2$ ), 95.2 (C-4'), 111.5 (C-2, 6), 123.9 (C-2', 6'), 125.2 (C-3, 5), 138.1 (C-3', 5'), 143.5 (C-1), 152.6 and 152.6 (C-4, 1');  $m/z$  ( $\text{ESI}^+$ ) 352 ( $[\text{M}+\text{H}]^+$ , 100%); HRMS ( $\text{ESI}^+$ ) calculated for  $\text{C}_{14}\text{H}_{15}\text{N}_3\text{I}$   $m/z$   $[\text{M}+\text{H}]^+$ : 352.0305; found, 352.0315.

**(*E*)-4-((4'-Diethyl benzylphosphonate))diazenyl)-*N,N*-dimethylaniline 6e.**

Product **6e** was purified by silica column chromatography (eluent 1:1 petrol:EtOAc) to give an orange solid.  $R_f$  0.61 (1:1 petrol:EtOAc); m.p. 101-105 °C;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  416 (2500  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ );



$^1\text{dm}^3\text{cm}^{-1}$ );  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  2903 (C-H), 1599 (N=N), 1518, 1442, 1401, 1363 (C-N), 1350, 1156, 1136 (P=O), 1025 (P-OEt), 956;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 1.25 (6H, t  $J$  7.1,  $\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)_2$ ), 3.07 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 3.21 (2H, d  $J$  22<sub>HP</sub>,  $\text{ArCH}_2\text{P}$ ), 4.00-4.06 (4H, m,  $\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)_2$ ), 6.75 (2H, app. d  $J$  9.1, H-2, 6), 7.40 (2H, app. dd  $J_{\text{HH}}$  7.6 and  $J_{\text{HP}}$  2.2, H-3', 5'), 7.80 (2H, d  $J$  7.6, H-2', 6'), 7.87 (2H, d  $J$  9.1, H-3, 5);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 16.3 ( $\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)_2$ ), 33.1 (d  $J$  138.2,  $\text{ArCH}_2\text{P}$ ), 40.3 ( $\text{N}(\text{CH}_3)_2$ ), 62.3 ( $\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)_2$ ), 111.5 (C-2, 6), 122.3 (C-2', 6'), 124.9 (C-3, 5), 130.3 (C-3', 5'), 132.9 (C-1'), 143.6 (C-1), 152.1 and 152.4 (C-4 and C-4');  $m/z$  ( $\text{ESI}^+$ ) 751 ( $[\text{2M}+\text{H}]^+$ , 100%), 376 ( $[\text{M}+\text{H}]^+$ , 40%); HRMS ( $\text{ESI}^+$ ) calculated for  $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_3\text{P}$   $m/z$   $[\text{M}+\text{H}]^+$ : 376.1785; found, 376.1786.

**(*E*)-4-((4'-Aminophenyl))diazenyl)-*N,N*-dimethylaniline 6f.**

Product **6f** was purified by silica column chromatography (eluent 10:1 petrol:EtOAc to EtOAc) and was isolated as an dark brown oily solid that was contaminated with an unknown impurity.  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ )/nm 413 (5980  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ );  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  3336 (N-H), 2917 (C-H), 1599, 1517, 1362 (C-N), 1149, 823;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 3.08 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 6.76 (2H, app. d  $J$  9.1, H-2, 6), 6.92 (2H, app. d  $J$  8.8, H-3', 5'), 7.79 (2H, app. d  $J$  8.8, H-2', 6'), 7.84 (2H, app. d  $J$  9.1, H-3, 5);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 40.4 ( $\text{N}(\text{CH}_3)_2$ ), 115.5 (C-2, 6), 116.6 (C-3', 5'), 124.0 (C-2', 6'), 124.5 (C-3', 5'), 143.6 (C-1), 147.5 (C-4'), 152.0 (C-1'), 157.2 (C-4);  $m/z$  ( $\text{ESI}^+$ ) 241 ( $[\text{M}+\text{H}]^+$ , 25%).

**(*E*)-4-((4'-Phenylacetic acid))diazenyl)-*N,N*-dimethylaniline 6g.**

Product **6g** was purified by silica column chromatography (eluent 6:1 petrol:EtOAc to 1:5 MeOH:EtOAc) and isolated as a black solid.  $R_f$  0.38 (1:6 petrol:EtOAc); m.p. 166-168 °C;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_3)/\text{nm}$  415 (10000  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ );  $\nu_{\text{max}}/\text{cm}^{-1}$  2918, 1709 (C=O), 1599 (N=N), 1517, 1357 (C-N), 1250, 1138, 820;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 3.10 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 3.72 (2H, s,  $\text{ArCH}_2\text{COOH}$ ), 6.85 (2H, app. d  $J$  9.1, H-2, 6), 7.47 (2H, app. d  $J$  8.5, H-2', 6'), 7.80 (2H, app. d  $J$  8.5, H-3', 5'), 7.85 (2H, app. d  $J$  9.1, H-3, 5);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 39.8 ( $\text{N}(\text{CH}_3)_2$ ), 40.6 ( $\text{ArCH}_2\text{COOH}$ ), 111.9

(C-2, 6), 122.3 (C-3', 5'), 125.1 (C-3, 5), 130.4 (C-2', 6'), 137.0 (C-4'), 143.8 (C-1), 132.4 (C-1'), 153.2 (C-4), 205.8 ( $\text{C}=\text{O}$ );  $m/z$  ( $\text{ESI}^+$ ) 306 ( $[\text{M}+\text{Na}]^+$ , 30%); HRMS ( $\text{ESI}^+$ ) calculated for  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_2$   $m/z$   $[\text{M}+\text{Na}]^+$ : 306.1213; found, 306.1206.

### **1,3-Bis(4-iodophenyl)triaz-1-ene 7.**

Product **7** was generated as a pale yellow solid as a by-product in the reaction of *N,N*-dimethylaniline with the iodo diazonium salt.  $R_f$  0.68 (10:1 petrol:EtOAc); mp 170-173 °C;  $\nu_{\text{max}}$ (neat)/ $\text{cm}^{-1}$  3200, 2923 (C-H), 2853 (C-H), 1586, 1501, 1476;  $\delta_{\text{H}}$  (100 MHz,  $\text{CDCl}_3$ ) 7.14 (4H, AA'BB' d, ArH-2, 6, 2', 6'), 7.69 (4H, AA'BB' d, ArH-3, 5, 3', 5');  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 119.8 (ArC-2, 6, 2', 6'), 138.3 (ArC-3, 5, 3', 5'), other carbons not detectable due to contamination;  $m/z$  ( $\text{ESI}^-$ ) 447.9 ( $[\text{M}-\text{H}]^-$ , 100%); HRMS ( $\text{ESI}^-$ ) 447.8808 found, 447.8808 expected.

### **Procedure C: Diazonium salt formation and Solution coupling.**

The corresponding amine (1.00 eq) was dissolved solvent (EtOH or THF:H<sub>2</sub>O=1:1). 3M HCl (2.00 eq) was added into the mixture and stirred in ice-bath for 10 min. NaNO<sub>2</sub> (1.20 eq) dissolved in approximately 1 mL H<sub>2</sub>O was then added into the cold mixture. The mixture was stirred in ice-bath for 30 - 40 min before H-acid was performed to test for presence of diazonium salt. The diazonium salt reaction mixture was used immediately *in situ*.

*Alternative method:* The corresponding amine (1.00 eq) was added into a stirring solution of EtOH (15 mL) at 0 °C in the dark. Isopentyl nitrite (1.20 eq) was added, followed by tetrafluoroboric acid (2.00 eq) into the reaction mixture, which was then continued to be stirred at 0 °C in the dark for 50 mins. H- acid test was conducted to detect presence of diazonium functional group. The mixture was used directly.

NaOAc (246 mg, 3.00 mmol, 2.00 eq) was added into the diazonium salt mixture in ice bath and stirred for 5 min, before phenol (141 mg, 1.50 mmol, 1.00 eq) dissolved in 1 mL of THF [or dimethylaniline (1.50 mmol, 1.00 eq)] was added. The reaction mixture was then stirred for 18 h

before THF was removed *in vacuo*. The precipitated product was collected on a Büchner funnel, washed with H<sub>2</sub>O and dried. Alternatively, if there were no precipitated product formed, the reaction mixture was extracted with DCM. The combined organic layers were dried over MgSO<sub>4</sub>, concentrated and purified using flash column chromatography

#### Synthesis of **N,N**-dimethyl-4-(phenyldiazenyl)aniline **11a**.

Using Procedure C, aniline **9a** (0.14 mL, 1.50 mmol, 1.00 eq) was reacted with *N,N*-dimethylaniline **8a** (0.14 mL, 1.50 mmol, 1.00 eq) in 1 mL THF to give the product **11a** (331mg, 98%) as an orange-yellow solid; m.p.: 105 -107 °C (lit. 111 °C);  $\nu_{\text{max}}/\text{cm}^{-1}$  2914, 1600 (C=C), 1564, 1516, 1407, 1364, 1139, 821  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.91 (2H, d,  $J$  = 8.5 Hz, H-3), 7.86 (2H, d,  $J$  = 7.6 Hz, H-6), 7.48 (2H, t,  $J$  = 7.3 Hz, H-7), 7.39 (1H, tt,  $J$  = 7.3, 1.7 Hz, H-8), 6.79 (2H, d,  $J$  = 9.1 Hz, H-2), 3.11 (6H, s, H-9);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 153.2 (C<sub>quat</sub>), 152.4 (C<sub>quat</sub>), 143.6 (C<sub>quat</sub>), 128.3 (C-8), 128.9 (C-7), 124.9 (C-3), 122.1 (C-6), 111.4 (C-2), 40.2 (C-9). HRMS (ESI<sup>+</sup>) calculated for C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>  $m/z$  [M+H]<sup>+</sup>: 226.1339; found: 226.1342.

#### Synthesis of 4-((4'-(dimethylamino)phenyl)diazenyl)phenyl)methanol **11c**.

Using Procedure C, 4-aminobenzyl alcohol **9c** (185 mg, 1.50 mmol, 1.00 eq) was reacted with *N,N*-dimethylaniline **8a** (0.14 mL, 1.50 mmol, 1.00 eq) in 1 mL THF to give the product **11c** (368 mg, 96%.) as a bright orange solid; m.p.: 195 – 197 °C;  $\nu_{\text{max}}/\text{cm}^{-1}$  3352, 1976, 1609 (C=C), 1555 (N=N), 1522, 1442, 1374, 1231, 11588, 1051 (C-O)  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) 7.78 (2H, d,  $J$  = 9.0 Hz, H-2'), 7.75 (2H, d,  $J$  = 8.3 Hz, H-2), 7.46 (2H, d,  $J$  = 8.3 Hz, H-3), 6.83 (2H, d,  $J$  = 9.1 Hz, H-3'), 5.31 (1H, t,  $J$  = 5.6 Hz, -OH), 4.57 (2H, d,  $J$  = 5.6 Hz, H-5), 3.05 (6H, s, H-5') ;  $\delta_{\text{C}}$  (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) 52.4 (C<sub>quat</sub>), 151.3 (C<sub>quat</sub>), 144.3 (C<sub>quat</sub>), 142.5 (C<sub>quat</sub>), 127.0 (C-3), 124.6 (C-2'), 121.6 (C-2), 111.5 (C-3'), 62.5 (C-5), 39.8 (C-5'). HRMS (ESI<sup>+</sup>) calculated for C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>O  $m/z$  [M+H]<sup>+</sup>: 256.14444; found: 256.14410.

#### Synthesis of 4-((4'-(dimethylamino)phenyl)diazenyl)benzoic acid **11d**.

Using Procedure C, 4-aminobenzoic acid **9d** (206 mg, 1.50 mmol, 1.00 eq) was reacted with *N,N*-dimethylaniline **8a** (0.14 mL, 1.50 mmol, 1.00 eq) in 1 mL THF to give the product **11d** (394 mg, 97%.) as a bright red solid; m.p.: >250 °C (lit. 179-182°C);  $\nu_{\max}/\text{cm}^{-1}$  2822, 1994, 1676 (C=O), 1594 (C=C), 1556 (N=N), 1421, 1361, (C-N), 1252, 1136  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CD}_3\text{SOCD}_3$ ) 13.07 (1H, broad s, -OH), 8.07 (2H, d,  $J = 8.5$  Hz, H-3), 7.83 (2H, d,  $J = 8.5$  Hz, H-2), 7.82 (2H, d,  $J = 9.3$  Hz, H-2'), 6.84 (2H, d,  $J = 9.3$  Hz, H-3'), 3.07 (6H, s, H-5');  $\delta_{\text{C}}$  (100 MHz,  $\text{CD}_3\text{SOCD}_3$ ) 166.9 (-COOH), 1555.1 ( $\text{C}_{\text{quat}}$ ), 153.0 ( $\text{C}_{\text{quat}}$ ), 142.7 ( $\text{C}_{\text{quat}}$ ), 130.9 ( $\text{C}_{\text{quat}}$ ), 130.5 (C-3), 125.3 (C-2'), 121.7 (C-2), 111.6 (C-3'), 39.8 (C-5'). HRMS (ESI<sup>+</sup>) calculated for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$   $m/z$  [M+H]<sup>+</sup>: 270.12370; found: 270.12344.

#### Synthesis of 4-(phenyldiazenyl)phenol **12a**.

Using Procedure C, aniline **9a** (0.14 mL, 1.50 mmol, 1.00 eq) was reacted with phenol **8b** (141 mg, 1.50 mmol, 1.00 eq) in 1 mL THF to give the product **12a** as an orange-yellow solid m.p. 155 -157 °C (lit. 152 - 155°C) after purification by flash column chromatography, eluting product at Petrol 40-60: EA = 30:1.  $R_f = 0.54$  in Petrol 40-60:EA = 4:1; (244mg, 82% – when 1.00 eq of NaOAc used; and 280 mg, 95% - when 2.00 eq of NaOAc used;  $\nu_{\max}/\text{cm}^{-1}$  2161, 1977, 1582, 1503, 1413, 1268, 1219, 1142, 993  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz, MeOD) 7.81 – 7.84 (4H, m, H-3, 6), 7.44 – 7.48 (2H, m, H-7) 7.38 – 7.42 (1H, m, H-8), 6.92 (2H, app d,  $J = 8.8$  Hz, H-2);  $\delta_{\text{C}}$  (100 MHz, MeOD) 162.0 ( $\text{C}_{\text{quat}}$ ), 154.0 ( $\text{C}_{\text{quat}}$ ), 147.4 ( $\text{C}_{\text{quat}}$ ), 131.2 (C-8), 130.0 (C-7), 125.9 (C-3/6), 123.3 (C-3/6), 116.7 (C-2). HRMS (ESI<sup>+</sup>) calculated for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$   $m/z$  [M+H]<sup>+</sup>: 199.08659; found: 199.08676.

#### Synthesis of 4-((4'-(hydroxymethyl)phenyl)diazenyl)phenol **12c**.

Using Procedure C, 4-aminobenzyl alcohol **9c** (185 mg, 1.50 mmol, 1.00eq) was reacted with phenol **8b** (141 mg, 1.50 mmol, 1.00 eq) in 1 mL THF to give the product **12c** as a brown solid m.p. 198 - 200 °C; (264mg, 77% – when 1.00 eq of NaOAc used; and 297 mg, 87% - when 2.00 eq of NaOAc used);  $\nu_{\max}/\text{cm}^{-1}$  3385, 2160, 1594 (N=N), 1500, (C=C), 1238, 1199, 1142, 1103  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$

(400 MHz, MeOD) 7.80 – 7.83 (4H, m, H-2, 2'), 7.50 (2H, d,  $J = 8.6$  Hz, H-3'), 6.91 (2H, d,  $J = 9.0$  Hz, H-3), 4.68 (2H, s, H-5');  $\delta_{\text{C}}$  (100 MHz, MeOD) 162.1 (C<sub>quat</sub>), 153.4 (C<sub>quat</sub>), 147.5 (C<sub>quat</sub>), 145.3 (C<sub>quat</sub>), 128.5 (C-3'), 125.9 (C-2'), 123.4 (C-2), 116.7 (C-3), 64.8 (C-5'). HRMS (ESI<sup>+</sup>) calculated for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>  $m/z$  [M+H]<sup>+</sup>: 229.09715; found: 229.09715.

### Synthesis of 4-((4'-hydroxyphenyl)diazenyl)benzoic acid **12d**.

Using Procedure C, 4-aminobenzoic acid **9d** (206 mg, 1.50 mmol, 1.00eq) was reacted with phenol **8b** (141 mg, 1.50 mmol, 1.00 eq) in 1 mL THF to give the product **12d** as an orange-yellow solid, m.p. >250 °C (lit. 270 -280°C); (318mg, 88% – when 1.00 eq of NaOAc used; and 332 mg, 92% - when 2.00 eq of NaOAc used);  $\nu_{\text{max}}/\text{cm}^{-1}$  3542, 3447, 1663 (C=O), 1588 (N=N), 1500 (C=C), 1429, 1283, 1143, 912  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz, MeOD)  $\delta$  8.16 (2H,  $J = 8.8$  Hz, H-3), 7.89 (2H, d,  $J = 8.6$  Hz, H-2), 7.86 (2H, d,  $J = 8.8$  Hz, H-2'), 6.93 (2H, d,  $J = 8.8$  Hz, H-3');  $\delta_{\text{C}}$  (100 MHz, MeOD) 169.2 (C<sub>quat</sub>), 162.9 (C<sub>quat</sub>), 156.8 (C<sub>quat</sub>), 147.6 9 (C<sub>quat</sub>) 132.9 (C<sub>quat</sub>), 131.8 (C-3), 126.4 (C-2'), 123.2 (C-2), 116.8 (C-3'). HRMS (ESI<sup>+</sup>) calculated for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>  $m/z$  [M+H]<sup>+</sup>: 241.06077; found: 241.06173.

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