Synthesis of Orthogonal Push-Pull Chromophores *via* Click Reaction of Arylynamines

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Herein we report a catalyst-free 'click' reaction: metal-free [2+2] cycloaddition–retro-electrocyclisation (CA-RE) of arylynamines with sluggish acceptor tetracyanoquinodimethane (TCNQ) to provide orthogonal electron-push-pull light-harvesting small molecules: *N*-heterocyclic dicyanoquinodimethane-substituted methylene malononitrile. Ynamines are reactive alkynes and tend to induce over-reactions with the CA-RE adducts. The reactivity of arylynamines was balanced properly according to governing the electron-density of the nitrogen atom delocalised more over the aromatic rings than the triple bond.

Dicyanoquinodimethane (DCNQ)-substituted methylene malononitrile, a family of non-planar charge-transfer push-pull chromophores, have attracted considerable interest in recent years, owing to their intense nonlinear absorption feature and electron-accepting ability that rival the benchmark compounds tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ).[1] DCNQ derivatives, a tetracyano cyclohexa-2,5-diene-1,4-diylidene-expanded motif, can be obtained by simply mixing an electron-rich alkyne with TCNQ *via* a catalyst-free [2+2] cycloaddition–retro-electrocyclisation (CA-RE).[2]

[2+2] CA-RE of TCNE with 1-alkynyl triazenes or ynamides to construct tetracyanobutadienes (TCBD) have been reported by Severin and Trolez respectively.[3] However, for ynamines – alkynes directly connected to an nitrogen atom which strongly activates and polarises the triple bond, except for two successful cases of [2+2] CA-RE with TCNE discovered by Trolez,[3b] most [2+2] CA-RE reactions have not been successful, either a mixture of numerous inseparable products were obtained or no reaction occurred (Figure 1).[3c] As for [2+2] CA-RE with less reactive acceptor TCNQ, standard alkynes, *i.e.*, dialkylaminophenyl acetylene, were employed in most cases,[4] neither ynamides or ynamines were successful with TCNQ.[3b]

Herein, we report a catalyst-free [2+2] CA-RE of ynamines with the less reactive acceptor TCNQ to afford DCNQ-substituted methylene malononitrile **6**. Unlike ynamide bearing an electron-withdrawing group on amide to reduce electron-density of alkyne, ynamine, with the amino group adjacent to the alkyne moiety, rendering the triple bond more electron-rich, therefore tends to be less stable and correspondingly more reactive towards sluggish acceptor TCNQ in [2+2] CA-RE; However, ynamines will induce their over-reactions with CA-RE adducts and produce a complex mixture with the formation of multiple oligomers, leading to the desired adducts in poor yields.[3b]

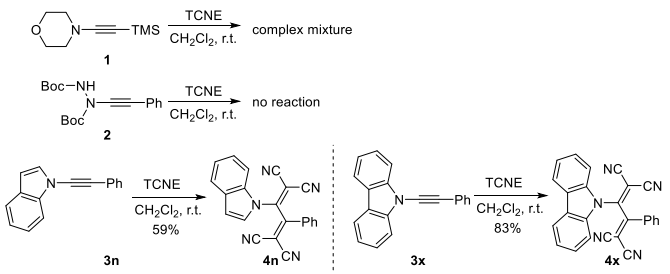

Figure 1. [2+2] CA-RE of ynamines or ynehydrazide with TCNE.

Herein we employ aryl ynamines for [2+2] CA-RE reaction with TCNQ. Owing to the electron lone pair of the amino group on arylynamines delocalising over aromatic rings, the electron-density of arylynamines is balanced properly between their reactivity and stability, *i.e.*, to maintain the alkyne electron-rich enough to react with the sluggish acceptor TCNQ, and at the meantime, to reduce over-reactions of ynamines.

We first evaluated the reactivity of the four different substrates – *N*-alkynyl hydrazide, ynamide, yndiamide and arylynamine[5] – with TCNE and TCNQ on [2+2] CA-RE respectively.[6] Most cases led to a mixture of inseparable products or decomposition, or no reaction occurred when reacting with TCNQ as it is not as reactive as TCNE.

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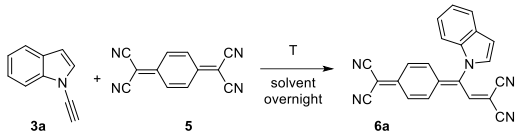
Noticeably, when arylated ynamine **3a** was employed with TCNQ, a moderate yield of [2+2] CA-RE product **6a** was obtained, accompanied by a complex mixture of inseparable adducts, probably resulting from over-reaction of **3a** with **6a**. We then studied the effect of variations of solvent and temperature (Table 1). The reaction was sluggish at room temperature with the majority of ynamine **3a** recovered, hence we heated it up at higher temperatures. Non-polar solvent (entry 1) and highly polar aprotic solvent (entry 10) as well as protic solvent (entry 11) proved less effective. For aprotic solvents with moderate polarity, the reaction proceeded to deliver the product **6a** in moderate yields (entries 2-6). Except for acetone that gave the lower yield (entry 4), a slight rise in yield was observed when the solvent polarity was increased. The yield increased to 84% in response to temperature enhancement (entries 6-8), but over-heating resulted in lower yield, accompanied by complex mixture and decomposition (entry 9).

Table 1. Optimisation of conditions.[a]



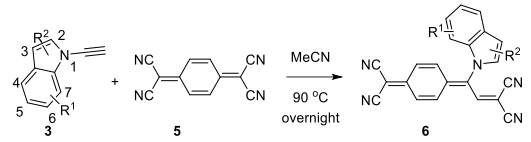
entry	T (°C)	solvent	yield[b] (%)
1	70	toluene	19
2	70	1,4-dioxane	52
3	70	ethyl acetate	56
4	70	acetone	33
5	70	1,2-dichloroethane	51
6	50	MeCN	56
7	70	MeCN	60
8	90	MeCN	84
9	100	MeCN	75
10	70	DMF	dec.[c]
11	70	EtOH	dec.[c]

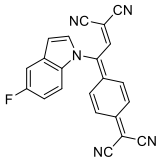
[a.] **3a** (0.2 mmol), TCNQ (0.2 mmol), solvent (2 mL), overnight. [b.] Isolated yield. [e.] dec. = decomposition.

Based on optimised results in Table 1, we used entry 8 as the reaction condition to explore the substrate scope of substituted terminal arylynamines **3** for investigation of electron delocalisation of the nitrogen atom in governing their relative reactivity on [2+2] CA-RE (Table 2). In general, the yields were lower than those obtained with standard electron-rich alkynes whose electron-donating group (EDG) are not directly linked to the triple bond. When phenyl ring of the indolyl moiety contained EDG at the *para*-position to the nitrogen atom, the [2+2] CA-RE delivered **6** in lower yields (**6e**, **6g**), accompanied by complex mixtures. This is presumably because of the increased electron-density of the nitrogen atom playing the role of activating the triple bond that induces over-reaction of ynamines with product **6**.

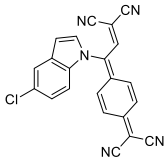
When R^1 was replaced by EWG at the *para*- (**6b**-**6d**) or *meta*-positions (**6h**) to the nitrogen atom, better yields were obtained. Noticeably, when the substituent was installed at the *ortho*- rather than *para*-position to the nitrogen, the yield was improved significantly from 33% to 53% (**6e** compared with **6f**). This could be explained by a sterical shielding of the dicyanovinyl moiety exerted by methyl group, which prevents decomposition of the product during the reaction. Compared to indole-derived ynamine, carbazole-derived ynamine **3j**, with the electron pair of the nitrogen atom delocalised more widely over aromatic rings than the triple bond, delivered a high yield of product **6j**. As for the pyrrole moiety, introducing an alkyl substituent provided **6i** at moderate yield (61%); However, substrates with aryl groups that exert greater steric hindrance underwent more complicated reactions by generating complex mixtures (**3k**-**3m**).

Table 2. Substrate exploration with respect to terminal arylynamines.[a]

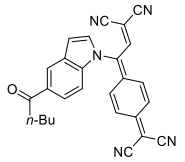




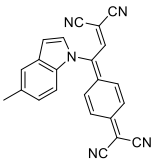
6b 54% (R^1 = F at C-5, R^2 = H)



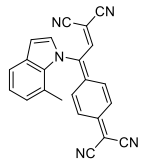
6c 44% (R^1 = Cl at C-5, R^2 = H)



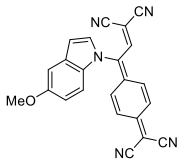
6d 50% (R^1 = C(O)*n*-Bu at C-5, R^2 = H)



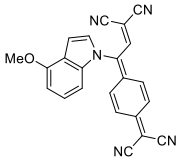
6e 33% (R^1 = Me at C-5, R^2 = H)



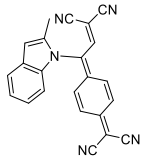
6f 53% (R^1 = Me at C-7, R^2 = H)



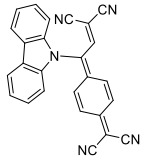
6g 30% (R^1 = OMe at C-5, R^2 = H)



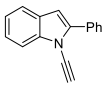
6h 43% (R^1 = OMe at C-4, R^2 = H)



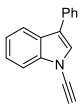
6i 61% (R^1 = H, R^2 = Me at C-2)



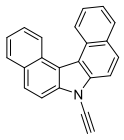
6j 74% (carbazole ynamine)



3k[b]



3l[b]



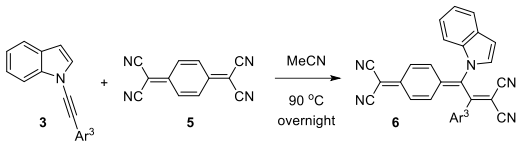
3m[b]

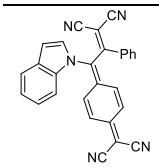
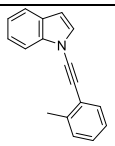
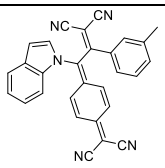
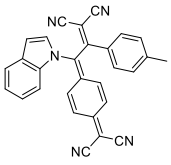
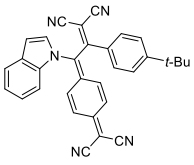
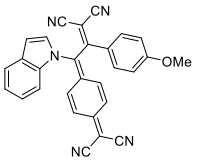
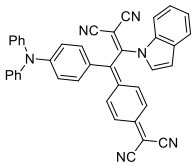
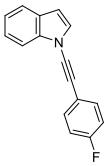
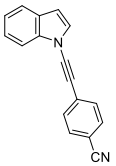
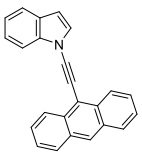
[a.] Ynamine (0.2 mmol) and TCNQ (0.2 mmol) in acetonitrile (0.1 M), 90 °C, overnight; Yields are for the isolated products. [b.] Complex mixture was formed.

We further explored the electron-density of arene in balancing the reactivity of internal arylynamines (Table 3). The ones with EDG on Ar^3 afforded the desired products in moderate to good yields (entries 4-7) with triphenylamino derivative achieving 74% yield: the regioselectivity of **6t** is inverted in entry 7.[7,1a,4b] By contrast,

ynamines with EWG on Ar^3 gave low yield of the products with the majority of complex mixtures of inseparable adducts (entries 8 and 9). The substrates were restricted to *para*-substituted aryl groups, [2+2] CA-RE of **3** containing *ortho*- or *meta*-substitute is more complicated with complex mixtures (entries 2, 3 and 10).

Table 3. Substrate exploration with respect to internal arylynamines.[a]



		
entry 1, **6n** 48% (Ar^3 = Ph)	entry 2, **3o** complex[b]	entry 3, **6p** 24% (Ar^3 = *m*-tolyl)
		
entry 4, **6q** 57% (Ar^3 = *p*-tolyl)	entry 5, **6r** 43% (Ar^3 = *p*-*t*-Bu-C_6H_4)	entry 6, **6s** 40% (Ar^3 = *p*-OMe-C_6H_4)
		
entry 7, **6t** 74% (Ar^3 = *p*-Ph_2N-C_6H_4)	entry 8, **3u** complex[b]	entry 9, **3v** complex[b]
		
entry 10, **3w** complex[b]		

[a.] Ynamine (0.2 mmol) and TCNQ (0.2 mmol) in acetonitrile (0.1 M), 90 °C, overnight; Yields are for the isolated products. [b.] Complex mixture was formed.

The configuration of the newly-formed dicyanovinyl group was confirmed by X-ray crystal structure of **6a**, which revealed that the alkene is formed as the *s-trans* conformation of diene (Figure 2).[8a,b] This is probably due to steric hindrance that precludes the quinodimethane moiety from adopting the s-*cis* conformation. The two dicyanovinyl groups are not in the same plane, with the dihedral angle of 24.9°. The torsion angle measured between indolyl and dicyanovinyl group is 82.3° (see Table S4 in SI), displaying almost orthogonal push-pull planes.

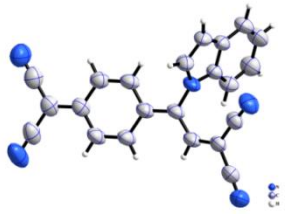
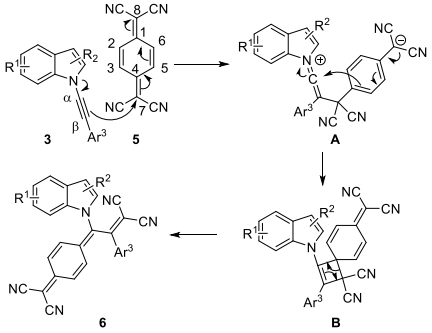


Figure 2. X-ray crystal structure of **6a** showing thermal ellipsoids at the 50% probability level. CCDC 2034942

For this [2+2] CA-RE reaction, we propose the following mechanism (Scheme 1). The first step involves a nucleophilic addition of ynamine **3**'s β-carbon at the C-7 of TCNQ regioselectively, determined by aromatisation as the driving force, to form an zwitterionic intermediate **A** containing an indolyl keteniminium moiety and aromatic resonance structure.[9] This is followed by an intramolecular nucleophilic attack of dicyano phenyl methanide to the highly electrophilic keteniminium to generate a highly strained cyclobutene **B**, which subsequently undergoes a retroelectrocyclisation to deliver product **6**.



Scheme 1. Proposed mechanism for [2+2] CA-RE of arylynamines

Arylynamine **3a** was applied on a larger scale to test reproducibility of [2+2] CA-RE (Figure 3). It resulted in a moderate yield with incomplete conversion of **3a**, and a complex mixture of inseparable adducts was formed. Scalability is challenging according to the developed protocol.

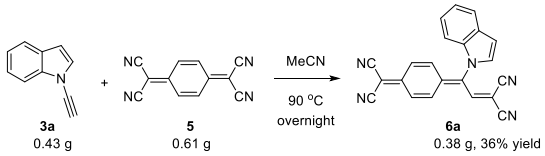


Figure 3. Scalability of the reaction.

To evaluate products' electronic property, we used **6a** as a model to record its cyclic voltammogram (Figure 4). The three cycles display gradual decrease in peak currents, indicating decreased reaction rate. This could arise from gradual consumption of our compound around the electrode which results in fewer species to oxidise / reduce on the anodic / cathodic scan.[10] It exhibits three reversible one-electron reduction waves at potentials of approximately 3.17, 2.8 and 2.41 V vs. Li/Li^+, *i.e.*, -0.56, -0.93 and -1.32 V vs. Fc/Fc^+. These potentials are indicative of their electron super-accepting properties of dicyanovinyl moieties and indolium which are subsequently reduced with one electron each time.[11] We observed three oxidation waves with anodic potential peaks at 3.15, 3.80 and 4.21 V vs. Li/Li^+, *i.e.*, -0.58, 0.07 V vs. Fc/Fc^+ that may

be assigned to the subsequent oxidation of the two dicyanomethanides, and 0.48 V vs. Fc/Fc^+ assigned to oxidation of indolyl unit which indicates a similar electron-donating ability with that of *N*,*N*-dialkylanilino DCNQ (0.42 V vs. Fc/Fc^+) and a stronger electron-donating character than that of Ts-amidyl TCBD (1.24 V vs. Fc/Fc^+).[8,12b] This can be attributed to the formation of a more stabilised cationic indolium radical compared with the cationic amidyl radical.

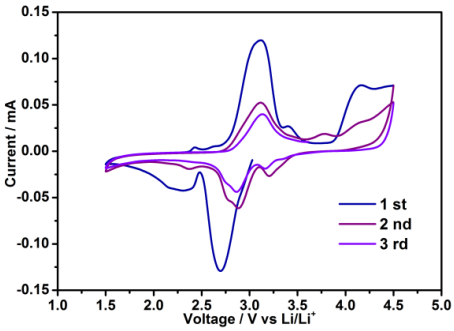


Figure 4. Cyclic voltammogram of compound **6a** in DEME-TFSI ionic liquid with LiTFSI (1 mmol / g) as the supporting electrolyte and a lithium foil as the reference electrode; the potentials are reported relative to Li/Li^+.[13]

The UV/Vis absorption properties of compounds **6** are dependent on the nature of the group linked to the methylene malononitrile moiety (Figure 5),[12,14] using **6a**, **6n** and **6t** as π-electron D-A models. Compounds **6** exhibit different absorption spectra in the visible range, with **6a**'s absorption maxima at λ = 419 and 444 nm. By contrast, **6n** and **6t** present notable features extending throughout the visible range. **6n** exhibits a large new absorption band at longer wavelengths between ca. 450 and 630 nm with a maximum at 519, 571 nm (ε = 2.31, 2.30 x 10^4 L / (mol × cm) respectively). Even more remarkable is a wide-band absorption of **6t** covering NIR regions with a maximum of wavelength at 677 nm (ε = 2.65 x 10^4 L / (mol × cm)). These extremely broad and featureless bands may be assigned to an ICT transition between the indolyl donor to the CN-containing acceptor moieties.[8]

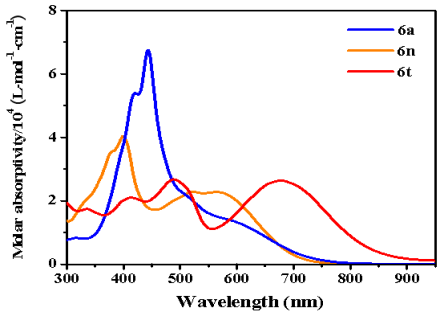


Figure 5. UV-visible absorption spectra of compounds **6a**, **6n** and **6t** in tetrahydrofuran.

In conclusion, we explored the scope and limitations of a catalyst-free [2+2] CA-RE of arylynamines with TCNQ. *N*-heterocyclic DCNQ-substituted methylene malononitrile were obtained in moderate to good yields. This synthetically convenient approach will heighten valuable potential towards the synthesis of light-harvesting molecules for potential applications in optoelectronic devices.[15]

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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