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# Novel Photo-induced Coupling Reactions of 9-Fluorenylidene-malononitrile or 1,1-Diphenyl-2,2-dicyanoethylene with 10-Methyl-9,10-dihydroacridine. A Study on the Photophysics of the Reaction

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9-Fluorenylidene-malononitrile (FDCN) or 1,1-diphenyl-2,2-dicyanoethylene (DPCN) reacted with 10-methyl-9,10-dihydroacridine (AcrH<sub>2</sub>) under irradiation ( $\lambda > 320$  nm) to give coupling products. In order to gain further insight into the mechanism of the photo-induced reaction, the photophysics of the reactions of FDCN or DPCN with AcrH<sub>2</sub> have been investigated by using UV-vis spectroscopy, fluorescence spectroscopy, excitation spectroscopy and time-resolved fluorescence spectroscopy, respectively. The results show that FDCN or DPCN interacts with AcrH<sub>2</sub> in the ground states to form a charge transfer complex, which further reacts to give the coupling product upon irradiation.

**Keywords** photo-induced coupling reaction, photophysics, ground state complex

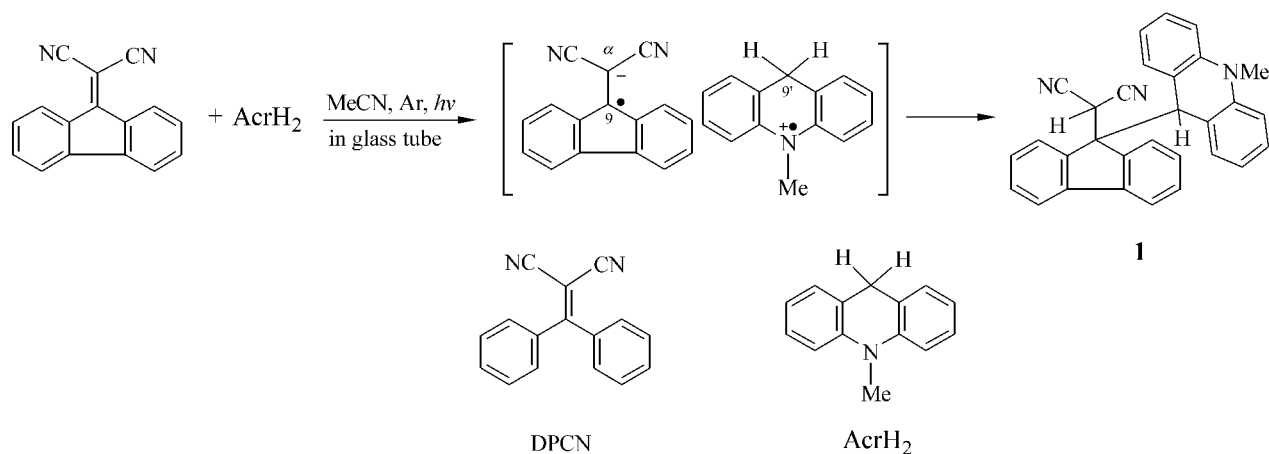
## Introduction

It was reported<sup>1</sup> that novel photo-induced coupling re-

action of 9-fluorenylidene-malononitrile (FDCN) with 10-methyl-9,10-dihydroacridine (AcrH<sub>2</sub>) took place via an electron transfer-proton transfer-radical coupling pathway to give 9-dicyanomethyl-9-(10'-methyl-9'-acridinyl)fluorene (**1**) (Scheme 1). Similarly, the photo-induced reaction of 1,1-diphenyl-2,2-dicyanoethylene (DPCN) with AcrH<sub>2</sub> also produced a coupling product.<sup>2</sup> These reactions are rather scarce with reduced nicotinamide adenine dinucleotide (NADH) analogues,<sup>3</sup> since the formal hydride transfer from NADH models usually takes place via electron transfer-proton transfer-electron transfer or electron transfer-hydrogen abstraction mechanism.<sup>4</sup>

In order to gain deeper insight into the mechanism of the photo-induced coupling reactions, we have investigated the photophysics of the reactions of FDCN or DPCN with AcrH<sub>2</sub>, respectively, and the results show that FDCN or DPCN interact with AcrH<sub>2</sub> in the ground states.

Scheme 1



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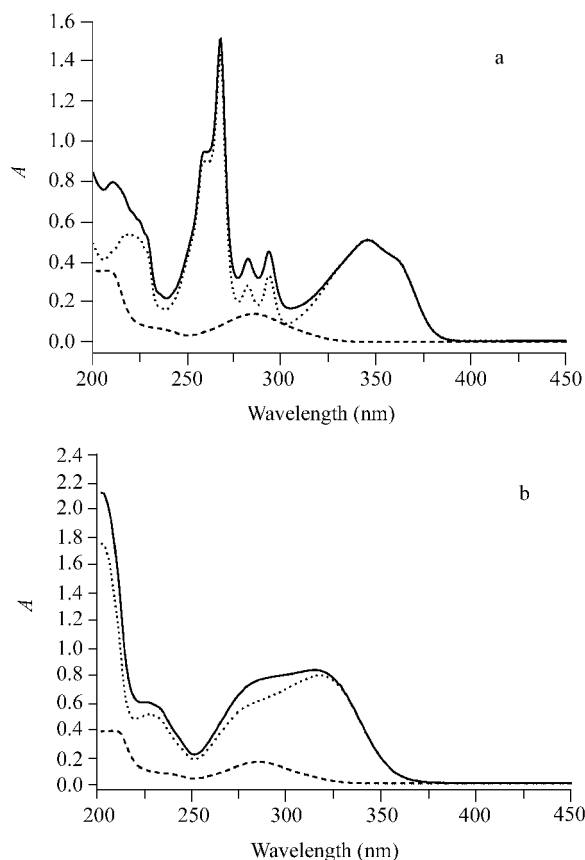
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## Experimental

UV-vis absorption spectra were measured on a Perkin Elmer UV-vis Spectrometer Lambda Bio 20. Fluorescence spectra were recorded on a Perkin Elmer Luminescence Spectrometer LS 50B. Fluorescence lifetimes were determined on a FLS920 Spectrometer (Edinburgh Instruments). AcrH<sub>2</sub>, FDCN and DPCN were prepared according to the reported method.<sup>5,6</sup> HPLC grade acetonitrile was dried and distilled over CaH<sub>2</sub> before use. The samples were purged with argon for at least 15 min before measurement.

## Results and discussion

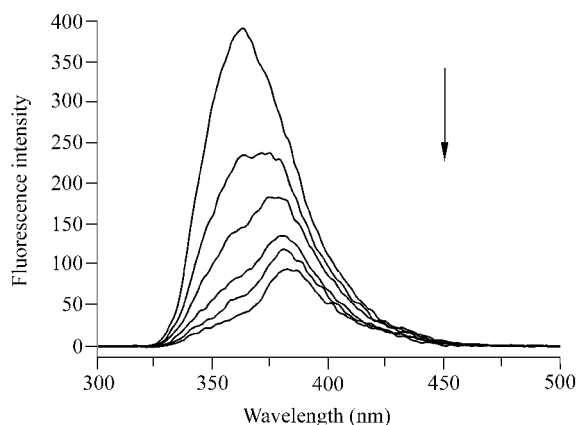
The UV-vis absorption spectra of AcrH<sub>2</sub> with FDCN or DPCN in acetonitrile solution were measured, respectively (Fig. 1). For comparison, the absorption spectra of AcrH<sub>2</sub>, FDCN and DPCN were separately measured and



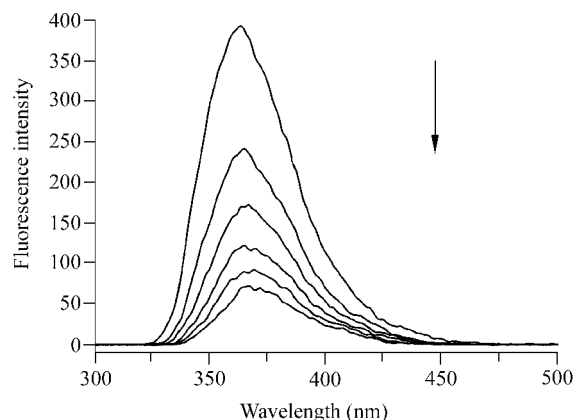
**Fig. 1** (a) Absorption spectra of AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) (-----), FDCN ( $5 \times 10^{-5}$  mol/L) (.....) and AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) with FDCN ( $5 \times 10^{-5}$  mol/L) (—) in CH<sub>3</sub>CN solution at room temperature; (b) Absorption spectra of AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) (-----), DPCN ( $6 \times 10^{-5}$  mol/L) (.....) and AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) with DPCN ( $6 \times 10^{-5}$  mol/L) (—) in CH<sub>3</sub>CN solution at room temperature.

also shown in Fig. 1. It can be seen that the spectra of AcrH<sub>2</sub> with FDCN and that of AcrH<sub>2</sub> with DPCN are practically identical with the summation of the spectra of AcrH<sub>2</sub> and FDCN and that of AcrH<sub>2</sub> and DPCN, respectively.

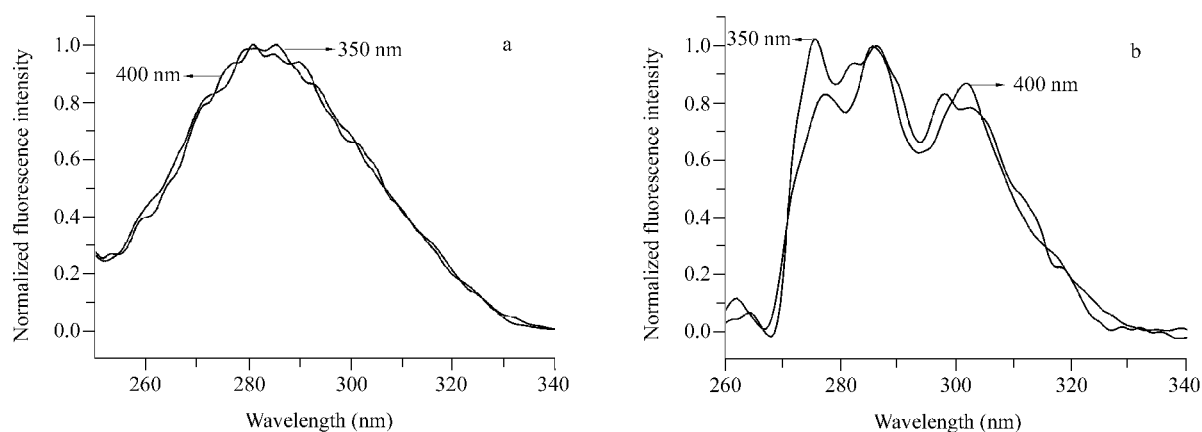
However, the fluorescence spectra of AcrH<sub>2</sub> in CH<sub>3</sub>CN differed significantly upon introducing increasing amounts of FDCN or DPCN into the solution when excited at  $\lambda = 284$  nm, as shown in Figs. 2 and 3, respectively. In CH<sub>3</sub>CN solution AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) exhibits the emission maximum at  $\lambda = 363$  nm. In control experiments, both FDCN and DPCN in CH<sub>3</sub>CN display no emission upon excitation with  $\lambda = 284$  nm. With increasing the concentration of FDCN or DPCN in the solution of AcrH<sub>2</sub> in acetonitrile, the fluorescence of AcrH<sub>2</sub> was gradually quenched and the emission peak displayed a red-shift of 19.25 nm for FDCN and 4.16 nm for DPCN, respectively, indicating that there may exist some interactions between AcrH<sub>2</sub> and FDCN or DPCN.



**Fig. 2** Fluorescence spectra of AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) in CH<sub>3</sub>CN solution in the presence of FDCN (0,  $1 \times 10^{-5}$ ,  $2 \times 10^{-5}$ ,  $3 \times 10^{-5}$ ,  $4 \times 10^{-5}$ ,  $5 \times 10^{-5}$  mol/L) with excitation of 284 nm at room temperature.



**Fig. 3** Fluorescence spectra of AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) in CH<sub>3</sub>CN solution in the presence of DPCN (0,  $2 \times 10^{-5}$ ,  $4 \times 10^{-5}$ ,  $6 \times 10^{-5}$ ,  $8 \times 10^{-5}$ ,  $1 \times 10^{-4}$  mol/L) with excitation of 284 nm at room temperature.



**Fig. 4** (a) Normalized curves of excitation spectra of AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) monitored at 350 nm and 400 nm at room temperature, respectively; (b) Excitation spectra of AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) in the presence of FDCN ( $5 \times 10^{-5}$  mol/L) monitored at 350 nm and 400 nm at room temperature, respectively.

In order to seek the evidence of interactions between AcrH<sub>2</sub> and FDCN or DPCN, the excitation spectra of the fluorescence for AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) and AcrH<sub>2</sub> ( $1 \times 10^{-5}$  mol/L) with FDCN in CH<sub>3</sub>CN were measured (Fig. 4). In control experiments, FDCN, DPCN and CH<sub>3</sub>CN alone showed no excitation peak and the excitation spectra almost coincided with the base line. The excitation spectrum for AcrH<sub>2</sub> monitored at  $\lambda = 350$  nm (or 400 nm) corresponds to the UV-vis absorption spectrum of AcrH<sub>2</sub>, while the feature of the excitation spectrum for AcrH<sub>2</sub> with FDCN monitored at  $\lambda = 350$  nm (or  $\lambda = 400$  nm) is significantly different, and both display the different spectral shape and shift in comparison with the excitation spectrum for AcrH<sub>2</sub>. From these results it is suggested that there exist interactions between AcrH<sub>2</sub> and FDCN in the ground state. In other words, the bathochromic shift of emission originates from the pairing of AcrH<sub>2</sub> and FDCN, which exists prior to excitation. A similar behavior was observed for AcrH<sub>2</sub> with DPCN, indicating that AcrH<sub>2</sub> interacts with FDCN or DPCN to form a complex in the ground state, and exhibits complex emission upon excitation.

For the purpose of seeking further information on the complex formation, the fluorescence decay of AcrH<sub>2</sub> in CH<sub>3</sub>CN solution in the presence of FDCN or DPCN was studied. Before addition of FDCN or DPCN, the fluorescence emission of AcrH<sub>2</sub> at 370 nm decays monoexponentially with lifetime of 6.83 ns. Upon the addition of FDCN or DPCN into the solution, the lifetime remains constant throughout the titration and the quenching process is static in nature. These results show that AcrH<sub>2</sub> interacts with FDCN in the ground state to form a charge transfer complex. As a result, irradiation of AcrH<sub>2</sub> with FDCN gave the coupling product **1** (Scheme 1). The same rationale

may apply to the photo-induced reaction of AcrH<sub>2</sub> with DPCN.

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