1,5-Diaminonaphtalene is a Highly Performing Electron-Transfer Secondary-Reaction Matrix for Laser Desorption Ionization Mass Spectrometry of Indolenine-Based Croconaines

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ABSTRACT: Croconaine dyes are appealing molecules synthesized via the condensation of croconic acid and reactive electron-donating aromatic or heterocyclic systems. Here, matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS) investigation of indolenine-based croconaines is presented for the first time. Archetype proton-transfer matrices, such as 2,5-dihydroxybenzoic acid (DHB) and α-cyano-4-hydroxycinnamic acid (CHCA), 9-aminoacridine (9AA) as the protonating/deprotonating matrix, and electron-transfer (ET) secondary-reaction matrices, such as 1,5-diaminonaphthalene (DAN) and trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), were investigated. DHB, CHCA, and 9AA generate a mix of odd-electron molecular ions and protonated, sodiated, and potassiated adducts. Among the ET matrices, DAN was found to be capable of directing the ionization process toward the exclusive formation of odd-electron molecular ions M+ without fragmentation. MALDI tandem MS provides useful structural characterization of croconaine dyes, thus making identification very straightforward for all investigated compounds. Interestingly the fragmentation of bromo-containing croconaines revealed, for the first time, the gas-phase formation of a bromine cation [Br]+.© 2018 American Chemical Society

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1. INTRODUCTION

Croconaines are donor–acceptor–donor type zwitterionic compounds synthesized from croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione) via a one-pot condensation reaction with electron-rich (hetero)aromatic compounds or heterocyclic methylene-active bases. Croconaines exhibit narrow and intense absorption bands in the NIR, and their optical properties can be finely tuned either by changing the donor portions, conjugated to the croconic acid core, or by inserting diverse substituents on the donor moieties. Very recently, synthetic strategies leading to derivatives with tailored photochemical properties have been reviewed. Whereas their third-order nonlinear optical properties appear potentially useful for ultrafast optical devices, recently, a small library of indolenine-based croconaines differing for the substituents on the donor moieties has been synthesized and their molecular structure fully investigated (by density functional theory (DFT) calculations, NMR spectroscopy, and X-ray diffraction) together with their solid-state organization. Ambipolar semiconducting properties have been obtained in thin-film transistors, demonstrating indolenine-based croconaines as a new class of molecular materials for organic electronics. Chemical and structural characterization of croconaines is typically performed by 1H- and 13C NMR, IR spectroscopy, and X-ray diffraction. At present, mass spectrometry (MS)-based techniques appear still confined to a marginal role in characterizing croconaines. Indeed, electron or chemical ionization methods typically employed in gas chromatography (GC)-MS are useless since indolenine-based croconaines cannot be investigated by GC due to molecular masses well
above 400 Da. So far, electrospray ionization mass spectrometry (ESI-MS) has been only used to assess the molecular mass of the synthesized croconaines (typically detected as deprotonated molecules), whereas structural characterization studies by tandem or multistage MS are lacking.13,17,18 Note that the above-mentioned poor solubility of croconaines could hamper ESI MS measurement since the best suited solvent ensuring adequate solubility could not be fully compatible with the ESI source. To the best of our knowledge, matrix-assisted laser desorption/ionization (MALDI) MS has never been used, as model compounds, matrices is presented, compared, and discussed in the following.

Table 1. Summary of All Croconaines (1–6) Investigated by MALDI MSa

| Chemical structure of croconaine dyes | # Substituents | Chemical formula | Monoisotopic mass (Da) | LUMO (eV)b | HOMO (eV)b |
|--------------------------------------|----------------|-----------------|------------------------|------------|-----------|
| ![Chemical structure](image)         | 1              | C10H14N2O3      | 650.2938               | -3.86      | -5.02     |
| 2                                    | R1 = CH3, R2 = N + H | C11H16BrN2O3 | 650.2938               | -3.86      | -5.02     |
| 3                                    | R1 = NH2, R2 = N + H | C9H16N3O3      | 650.2938               | -3.86      | -5.02     |
| 4                                    | R1 = CH3, R2 = N + H | C10H14N2O3      | 650.2938               | -3.86      | -5.02     |
| 5                                    | R1 = NH2, R2 = N + H | C9H16N3O3      | 650.2938               | -3.86      | -5.02     |
| 6                                    | R1 = NH2, R2 = N + H | C9H16N3O3      | 650.2938               | -3.86      | -5.02     |

| ![Chemical structure](image)         | 2              | C10H14N2O3      | 650.2938               | -3.86      | -5.02     |
| 3                                    | R1 = CH3, R2 = N + H | C11H16BrN2O3 | 650.2938               | -3.86      | -5.02     |
| 4                                    | R1 = NH2, R2 = N + H | C9H16N3O3      | 650.2938               | -3.86      | -5.02     |
| 5                                    | R1 = NH2, R2 = N + H | C9H16N3O3      | 650.2938               | -3.86      | -5.02     |
| 6                                    | R1 = NH2, R2 = N + H | C9H16N3O3      | 650.2938               | -3.86      | -5.02     |

Energy levels of HOMO and LUMO were determined by cyclic voltammetry in CH3Cl solution. For experimental details, see ref 17.

As expected for analytes with extended aromatic π-electron systems, all investigated croconaines are characterized by particularly low IPs (around 5.3 eV), suggesting a facile direct photoionization process in the gas phase upon irradiation by Nd:YLF laser ( photon energy, 3.6 eV). Indeed, the LDI mass spectrum of, e.g., croconaine #5 (see Figure S1, Supporting Information) shows the distinct formation of a [M]+ radical ion at m/z 496 that can be easily rationalized invoking a two-photon ionization process.26 The absolute signal intensity is not particularly high, which is consistent with a broad and poor absorption band at the laser wavelength of 345 nm, too far from the absorption maximum at ca. 780 nm (Figure S2, Supporting Information). A similar behavior is shared by all other investigated compounds. The above LDI findings suggest that direct analyte photoionization should be likely expected also in MALDI experiments; however, due to the excess of matrix, such a process cannot play a significant role since secondary ionization of an analyte by a matrix is far more likely than the direct ionization of analyte, unless very high analyte/matrix ratios are used,29 which is not the case.

2. RESULTS AND DISCUSSION

2.1. Laser Desorption Ionization (LDI)-MS experiments. Indole derivatives croconaines investigated here are reported in Table 1 along with their chemical formula, substituent groups on each indolene moiety, and monoisotopic mass; note that all croconaines are symmetrical and differ by the donor substituents, namely, heteroatoms as chlorine (#3–5) and bromine (#2) or aromatic moieties as 4-phenoxy-phenyl (#1) and 4-nitro-phenyl (#6). Highest-occupied and lowest-unoccupied Kohn–Sham orbital (HOMO and LUMO) energy levels, previously estimated from cyclic voltammetry (CV) experiments,17 are also quoted, given their importance in rationalizing the laser desorption ionization mechanism (vide infra). Unfortunately, DFT calculations of HOMO and LUMO energy levels, which generally provide ionization potential (IP) and electron affinity (EA) values, respectively, in good agreement with the experimental data in a vacuum,26 are not available for the investigated compounds. It follows that HOMO and LUMO energy levels obtained by CV provide only rough (but still useful) estimates of IP and EA values mainly because the HOMO/LUMO energies are scaled in vacuum, whereas the reduction/oxygenation potentials are measured in solution.26,27

Figure 1 displays the positive-ion MALDI MS spectra of croconaine #1 using CHCA (a), DHB (b), and 9AA (c) as matrices. The base peak at m/z 761.302 in the MALDI spectrum obtained using CHCA as the matrix (plot (a)) was assigned to the protonated adduct [M + H]+. Interestingly, the coconum occurrence of an odd-electron molecular ion, M*+, at m/z 760.298, with a remarkably high yield (ca. 70%, see the inset of plot (a)) can be observed; since...
direct photoionization can provide only a marginal contribution (see the previous paragraph), the formation of $M^{+*}$ should be mainly due to secondary reactions, indicating that PT and ET are competing processes. Cationization by Na⁺ and/or K⁺ be mainly due to secondary reactions, indicating that PT and ET are competing processes. A small contribution of a K⁺ adduct also appears, (plot (c)) as matrices; the formation of sodiated adducts (see fi...<noinput>..."...Figure 1. Positive-ion mass spectra by MALDI-time-of-flight (ToF) of croconaine dye #1 (M, C₁₉H₁₆N₂O₆) obtained by using (a) CHCA, (b) DHB, and (c) 9AA as matrices. Enlarged isotopic patterns of the main peaks detected in each spectrum are shown in insets.

Table 2. Thermodynamic Data of Matrices Used in This Work for Croconaine Examination by MALDI MS

|            | CHCA     | DHB      | 9AA      | DCTB     | DAN      |
|------------|----------|----------|----------|----------|----------|
| PA (kcal/mol) | 201.0    | 204.4    | 233.4    | n.a      | 225.0    |
| EA (eV)     | 40.1     | 17.7     | 14.4     | 53.3     | -9.18    |
| IP (eV)     | 8.80     | 8.20     | 7.23     | 8.54     | 6.84     |

"PA: proton affinity, EA: electron affinity, IP: ionization potential. Data obtained by refs 23–30 and references herein. See ref 37. Data obtained by Mol-Instincts Chemical Property Database (https://www.molinstincts.com/home/index/)."
After isolating and fragmenting the molecular ion ([M]+ 582.001 (plot (3a)), dye (Figure S4, Supporting Information). Indeed, as reported in Figure 3, it was possible to detect the radical cation with nearly 100% yield, in the spectra of the croconaine dye main peak at a methyl radical (CH3), most likely from the dihydropyrrrole ring. The second abundant peak at m/z 730.55 could be generated by the alternative loss of neutral formaldehyde (CH2O), in which the croconic acid core may be involved, or more likely from a consecutive loss of another methyl radical (*CH3) from the second dihydropyrrrole ring. The ion cluster centered at m/z 667.20 can be correlated to the radical loss of phenol (C6H4O*). For the less intense ions in the spectrum, several hypothetical product ions can be proposed. For instance, the peak observed at m/z 415.20 can be explained by considering the breaking of the indolenine core. Also, product ions at m/z 361.19 and 345.20 are related to bond breaking in the gas phase on different points of the structure, which more likely involves the further loss of lateral substituents. The peak at m/z 93.06 is most likely due to the phenoxo ion arising from the side substituents.

Figure 3 shows the positive MALDI MS/MS spectrum of the croconaine dye #2 (isolation window ±5 m/z units) using DAN as the matrix. This compound contains two symmetrical substituents bearing bromide as a heteroatom. When fragmenting the ion cluster centered at m/z 582, two leading product ions were detected, respectively corresponding to the successive loss of two radical methyl moieties from the dihydropyrrrole rings, as occurred with dye #1 (see signals at m/z 567.07 and 552.14); an additional methyl loss can generate the small peak at m/z 537.14. The ion at m/z 330.08 could originate from different losses as its isotopic pattern appears to be an envelope of at least two contributions. For instance, it could be due to the neutral loss of bromobenzene (C6H5Br) from one side and bromide (Br) from the other substituent together with methyl loss or more likely it could be explained as the loss of the whole substituent 5-bromo-3,3-dimethylindoline from one side and methyl from the other symmetric side. The peak at m/z 276 is most likely generated from that at m/z 332 assigned as croconic moiety missing a methyl group upon loss of ethene-1,2-dione [C4O2].

Besides other low-intensity product ions likely generated by successive losses of water (18 Da) or methyl radical (15 Da), an interesting ion doublet was detected at m/z 78.94 and 80.93. According to both the accurate mass and isotopic pattern, this cluster can be easily attributed to bromine cation, [Br]+, formed via heterolytic cleavage. The use of the present ion species may appear anomalous since bromine follows the octet rule and usually is detected in a negative-ion mode as a bromide ion. Although much less intense, the product ions at m/z 501–503 are also evident following the initial loss of a bromine Br* radical (i.e., homolytic cleavage). The use of the same croconaine dye #2 and a PT matrix such as CHCA
(Figure S5, Supporting Information) provides no evidence of bromine cation. This is the first time that the Br⁺ has been described in a MALDI experiment but it is not completely unusual using other techniques, including inductively coupled plasma-MS and glow-discharge ionization source.

3. CONCLUSIONS

Here, we have reported for the first time that DAN can be successfully used as a matrix to explore intact croconaine dyes by means of MALDI MS in a positive-ion mode. The prevailing ionization process of croconaines by DAN seems to be an ET secondary-reaction mechanism, thus hindering the splitting of ion contribution to protonated and cationized adducts, as observed with other examined matrices. Tandem MS of the radical molecular ions was found to be very useful to characterize the structure of these dyes. The most singular result was observed with the gas-phase formation of bromine cation on croconaines bearing Br as heteroatom substituents. This outcome has never been reported before, at least under MALDI MS experimental conditions. It is plausible that DAN will be actively used as a major MALDI matrix in identifying novel croconaine dyes.

4. MATERIALS AND METHODS

4.1. Chemicals. Water, acetonitrile, methanol, chloroform, 1,5-diaminonaphthalene (DAN), trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), 2,5-dihydroxybenzoic acid (DHB), and α-cyano-4-hydroxycinnamic acid (CHCA) were obtained from Sigma-Aldrich (Milan, Italy), whereas 9-aminoacridine hemihydrate was purchased from Acros Organics (Morris Plains, NJ). All solvents used were of LC−MS grade. A Mass Standard Kit for calibration was purchased from AB Sciex (Ontario, Canada).

4.2. Instrumentation. All experiments were performed using a 5800 MALDI-ToF/ToF analyzer (AB Sciex, Darmstadt, Germany) equipped with a neodymium-doped yttrium lithium fluoride (Nd:YLF) laser (345 nm), in a reflection positive mode, with a typical mass accuracy of 10 ppm. In MS and MS/MS modes, 1000 laser shots were typically accumulated by a random rastering pattern, at laser pulse rates of 400 and 1000 Hz, respectively; each shown mass spectrum was averaged on at least five single mass spectra (1000 laser shots each). The laser fluences were within 1.9−2.6 J/m² depending on the matrix employed. MS/MS experiments were performed setting a potential difference of 1 kV between the source and the collision cell; ambient air was used as the collision gas with a medium pressure of 10⁻⁶ Torr. The delayed extraction time was set at 280 ns.

DataExplorer software 4.0 (AB Sciex) was used to control the acquisitions and to perform the initial elaboration of data, whereas SigmaPlot 11.0 was used to graph the final mass spectra. ChemDraw Pro 8.0.3 (CambridgeSoft Corporation, Cambridge, MA) was employed to draw chemical structures. Isotopic pattern contribution was generated by Xcalibur 4.0 with Foundation 3.1 (Thermo Fisher Scientific).

4.3. Croconaine Synthesis. Indolenine-based croconaines bearing different substituents on the donor moieties were synthesized following a protocol based on condensation of croconic acid (1 equiv) and of indolenine (2 equiv) in a refluxing mixture of toluene and butanol. Synthesis and characterization of croconaines #1−4 and #6 (see Table 1) were carried out in accordance with a previously reported procedure. Synthesis of the new croconaine #5, namely, 3-(5,7-difuoro-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl)-5-(5,7-difuoro-3,3-dimethyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione, is described in the Supporting Information.

4.4. Sample Preparation and MALDI MS Analysis. All investigated croconaines were dissolved in chloroform at a concentration of 2.0 mM. CHCA, DHB, and 9AA matrices were prepared in methanol at a concentration of 50 mM, whereas DAN and DCTB matrices were prepared in acetone at a concentration of 32 mM. Unless otherwise specified, 5 µL of each croconaine solution was mixed (1:1, v/v ratio) with matrix solution and 1 µL of mixture was spotted on the target plate, dried in the dark, and analyzed by MALDI MS.

WARNING: Caution should be reserved when handling DAN due to its possible carcinogenetic effects. Exposure to this compound should be minimized, and fume hoods should always be used.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02575.

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Notes

The authors declare no competing financial interest.

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