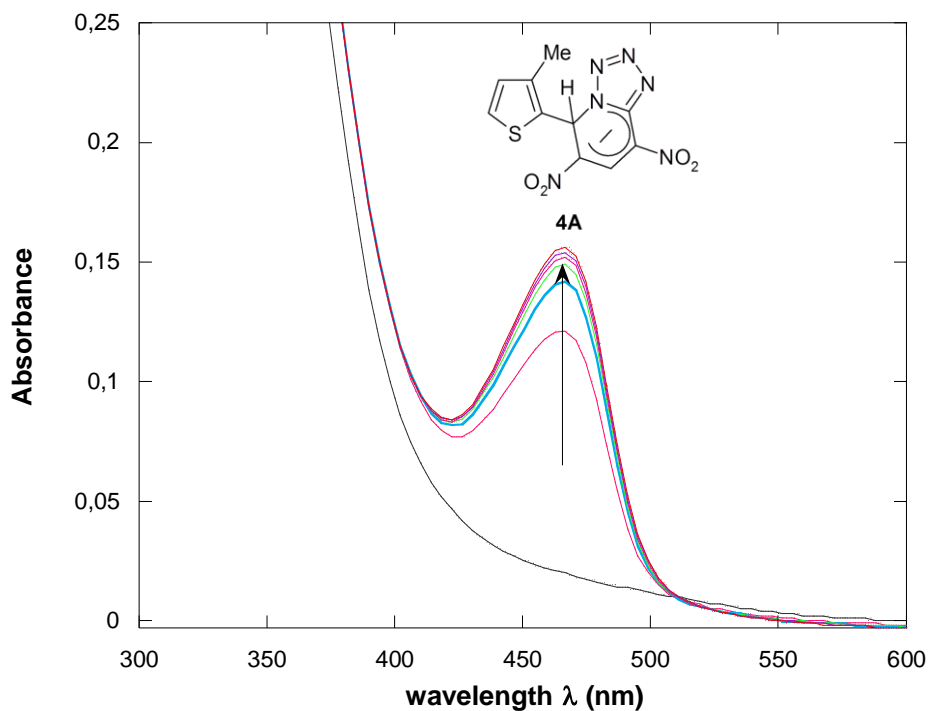# Supporting Information

Figure S.1. UV-visible spectrum of thiophene **1a** and the progressive evolution of the formation of product **4A** in acetonitrile at 20 ° C with [**1a**] = 1 mol L^{-1} and [**2a**] = 5.10-5 mol L^{-1}
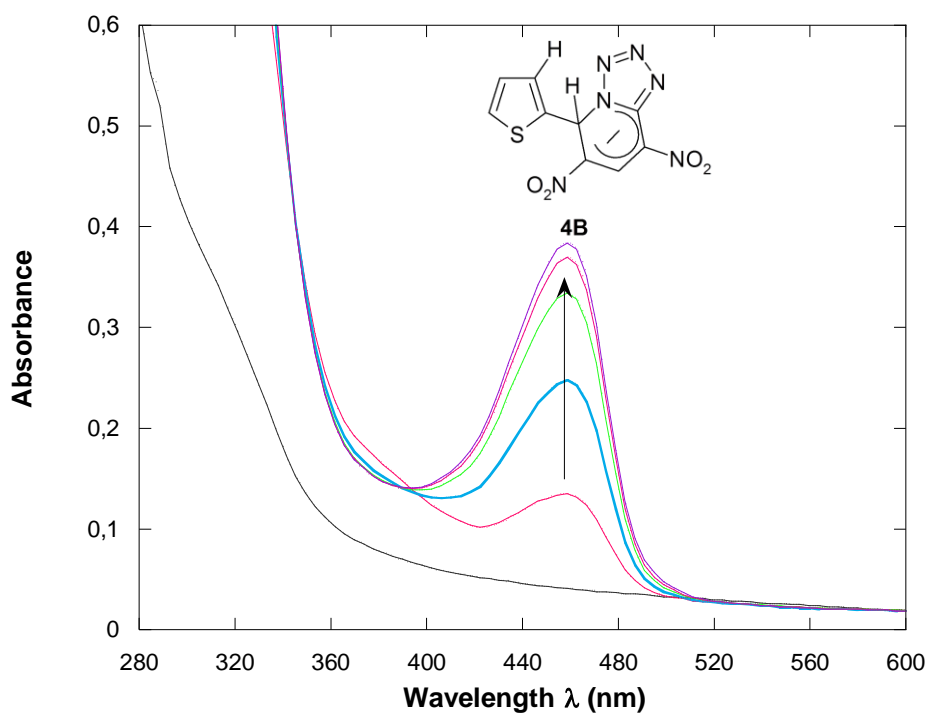

Figure S.2. UV-visible spectrum of thiophene **1b** and the progressive evolution of the formation of product **4B** in acetonitrile at 20 ° C with [**1b**] = 1 mol L^{-1} and [**2a**] = 5.10^{-5} mol L^{-1}

Table S.1-Influence of thiophene concentration **1a** on the pseudo-first order rate constants for formation of adducts **4A**, **5A**, **5D** and **5G** in acetonitrile and at 20 ° C.
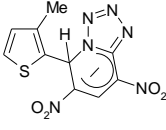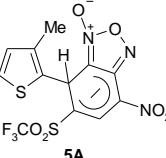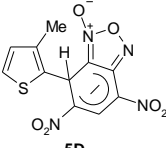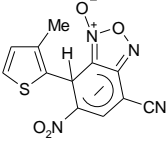
σ–adduct	[1a] (mol L^{-1})	k$_{obsd}$ (s^{-1})
  4A	1 5 x 10^{-1} 4 x 10^{-1} 1 x 10^{-1}	4.14 x 10^{-3} 2.05 x 10^{-3} 1.66 x 10^{-3} 5.26 x 10^{-4}
  5A	1 8 x 10^{-1} 6 x 10^{-1} 4 x 10^{-1}	2.71 x 10^{-3} 2.08 x 10^{-3} 1.68 x 10^{-3} 1.12 x 10^{-3}
  5D	1 6 x 10^{-1} 4 x 10^{-1} 2 x 10^{-1}	1.24 x 10^{-3} 8.01 x 10^{-4} 5.08 x 10^{-4} 2.81 x 10^{-5}
  5G	1 8 x 10^{-1} 6 x 10^{-1} 4 x 10^{-1}	3.50 x 10^{-5} 2.79 x 10^{-5} 1.89 x 10^{-5} 1.07 x 10^{-5}

Table S.2-Influence of thiophene concentration **1b** on the pseudo-first order rate constants for formation of adducts **4B**, **5B**, **5E** and **5H** in acetonitrile and at 20 ° C.
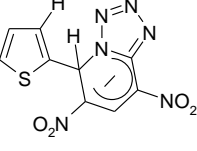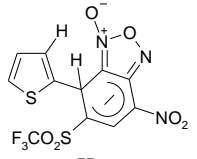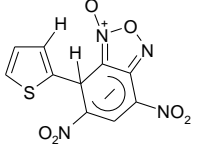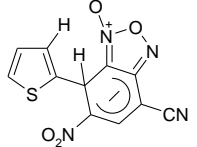
σ–adduct	[1b] (mol L^{-1})	k$_{obsd}$ (s^{-1})
  4B	1 5 x 10^{-1} 2 x 10^{-1} 1 x 10^{-1}	1.28 x 10^{-3} 6.39 x 10^{-4} 2.58 x 10^{-4} 1.29 x 10^{-4}
  5B	5 x 10^{-1} 4 x 10^{-1} 2 x 10^{-1} 1 x 10^{-1}	3.61 x 10^{-4} 2.86 x 10^{-4} 1.48 x 10^{-4} 7.36 x 10^{-5}
  5E	1 8 x 10^{-1} 5 x 10^{-1} 2 x 10^{-1}	3.42 x 10^{-4} 2.69 x 10^{-4} 1.67 x 10^{-4} 7.19 x 10^{-5}
  5H	1 8 x 10^{-1} 6 x 10^{-1} 4 x 10^{-1}	1.80 x 10^{-5} 1.56 x 10^{-5} 1.28 x 10^{-5} 9.92 x 10^{-6}

Table S.3-Influence of thiophene concentration **1c** on the pseudo-first order rate constants for formation of adducts **4C**, **5C**, **5F** and **5I** in acetonitrile and at 20 ° C.
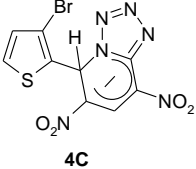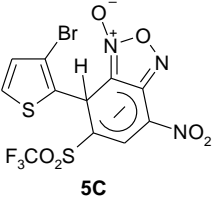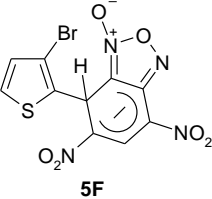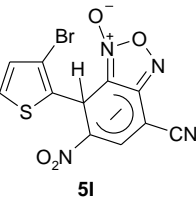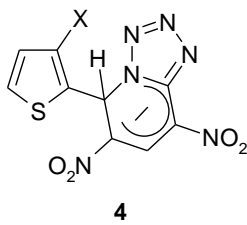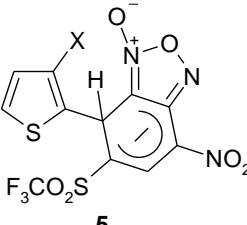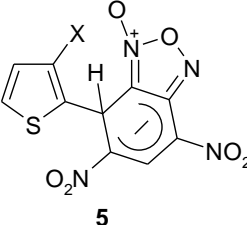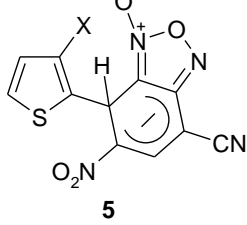
σ−adduict	[1c] (mol L^{-1})	k$_{obsd}$ (s^{-1})
4C	1 8 x 10^{-1} 6 x 10^{-1} 4 x 10^{-1}	3.36 x 10^{-4} 2.84 x 10^{-4} 2.05 x 10^{-4} 1.41 x 10^{-4}
5C	1 8 x 10^{-1} 6 x 10^{-1} 4 x 10^{-1}	2.27 x 10^{-4} 1.76 x 10^{-4} 1.33 x 10^{-4} 1.00 x 10^{-4}
5F	1 8 x 10^{-1} 6 x 10^{-1} 2 x 10^{-1}	1.09 x 10^{-4} 8.35 x 10^{-5} 6.75 x 10^{-5} 2.11 x 10^{-5}
5I	1 8 x 10^{-1} 6 x 10^{-1} 4 x 10^{-1}	4.53 x 10^{-6} 3.76 x 10^{-6} 2.69 x 10^{-6} 1.98 x 10^{-6}

Table-S.4- Values of λ_{max} and molar extinction coefficients ε for σ–adducts **4** and **5** in acetonitrile at 20 ° C.

σ–adduct		λ_{max} (nm)	ε (mol^{-1} L cm^{-1})
	4A (X = Me)	465	15400
	4B (X = H)	466	22400
	4C (X = Br)	467	17100
	5A (X = Me)	410	67700
	5B (X = H)	405	36300
	5C (X = Br)	410	87100
	5D (X = Me)	487	34500
	5E (X = H)	481	57300
	5F (X = Br)	481	16400
	5G (X = Me)	480	5900
	5H (X = H)	477	4230
	5I (X = Br)	476	5100