Supplementary Information

Highly fluorescent complexes with 3-isocyanoperylene and N-(2,5-di-tert-butylphenyl)-9-isocyno-perylen-3,4-dicarboximide

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IU CINQUIMA Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47071 Valladolid, Spain; and Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain.

Fig. S1  Absorption spectra of PMI-NC and their complexes 5a, 9a-12a, recorded in CHCl$_3$ solution ($\sim$10$^{-5}$ M) at room temperature

Fig. S2  Absorption spectra of Per-NC and their complexes 5b-11b, recorded in CHCl$_3$ solution ($\sim$10$^{-5}$ M) at room temperature

Fig. S3  Emission spectra of 11b in different solvents (ca.$10^{-5}$ M) at room temperature.

Fig. S4  Schematic representation of main expected transition in the absorption spectra of PMIH and perylene.

Table S1  Calculated absorption parameters (wavelengths in nm and their intensities) for R-X (R = PMI and Per) compounds in gas phase and chloroform solution.

Table S2  Calculated absorption peaks for [M(CO)$_5$(CNR)] (M = Cr, Mo, W; R = PMI, Per).

Fig. S5  $^1$H and $^{19}$F NMR spectra

Fig. S6  IR spectra

Fig. S7  Fluorescence decays in dichloromethane, at room temperature

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† Universidad de Valladolid

‡ Universitat de Barcelona
**Figure S1.** Absorption spectra of PMI-NC and their complexes 5a, 9a-12a, recorded in CHCl₃ solution (\(\sim 10^{-5}\) M) at room temperature

**Figure S2.** Absorption spectra of Per-NC and their complexes 5b-11b, recorded in CHCl₃ solution (\(\sim 10^{-5}\) M) at room temperature

**Fig. S3** Emission spectra of 11b in different solvents (ca.\(10^{-5}\) M) at room temperature.
Fig. S4 Schematic representation of main expected transition in the absorption spectra of PMIH and perylene.
**Table S1.** Calculated absorption parameters (wavelengths in nm, oscillator strength (f), and coefficients of the main contributions of the orbitals [in brackets]) for R-X (R = PMI and Per) compounds in gas phase and chloroform solution.

**Organics**

<table>
<thead>
<tr>
<th>λ (f)</th>
<th>Solvent</th>
<th>H</th>
<th>NC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMI-X</td>
<td>Gas phase</td>
<td>477 (0.61)</td>
<td>490 (0.69)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.62]</td>
<td>[0.61]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260 (0.09), 259 (0.11)</td>
<td>261 (0.19)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.48, 0.38], [0.44, 0.40]</td>
<td>[0.55, 0.23]</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>500 (0.77)</td>
<td>512 (0.86)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.63]</td>
<td>[0.63]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>262 (0.26)</td>
<td>263 (0.22)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.55, 0.15]</td>
<td>[0.51, 0.30]</td>
</tr>
<tr>
<td>Per-X</td>
<td>Gas phase</td>
<td>428 (0.36)</td>
<td>446 (0.44)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.62]</td>
<td>[0.62]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>253 (0.30)</td>
<td>257 (0.28)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.48, 0.36]</td>
<td>[0.48, 0.25]</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>442 (0.48)</td>
<td>465 (0.58)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.63]</td>
<td>[0.63]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>257 (0.51)</td>
<td>260 (0.44)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[0.50, 0.38]</td>
<td>[0.51, 0.22]</td>
</tr>
</tbody>
</table>

*a Coefficients are \([\pi_{HOMO} \rightarrow \pi^*_{LUMO}]\) for first transition in all cases, and \([\pi_{HOMO} \rightarrow \pi^*, \pi \rightarrow \pi^*_{LUMO}]\) for second band of perylene systems.*
(b) Chromium complexes

<table>
<thead>
<tr>
<th>λ (f)</th>
<th>[(PMI-NC)Cr(CO)₅]</th>
<th>[(PerNC)Cr(CO)₅]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<tr>
<td>Gas phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>λ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>518 (0.97)</td>
<td>π(PMI)_H → π*(PMI-NC)₅ [0.70]</td>
<td>π(Per)_H → π*(Per-NC)₅ [0.70]</td>
</tr>
<tr>
<td>281 (0.08)</td>
<td>π(CO) + πd → π*(CO)₅ [0.52]</td>
<td>π(Per)_H → π*(Per) [0.42]</td>
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<tr>
<td></td>
<td>π(CO) → π*(PMI-NC) [0.33]</td>
<td>πd → π*(Per) [0.26]</td>
</tr>
<tr>
<td></td>
<td>266 (0.09)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>π(CO) + πd → π*(PMI-NC) [0.54]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>π(PMI) → π*(PMI) [0.24]</td>
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</tr>
<tr>
<td>CHCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>λ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>536 (1.14)</td>
<td>π(PMI)_H → π*(PMI-NC)₅ [0.70]</td>
<td>π(Per)_H → π*(Per-NC)₅ [0.70]</td>
</tr>
<tr>
<td>282 (0.10)</td>
<td>π(CO) + πd → π*(CO)₅ [0.54]</td>
<td>π(Per)_H → π*(Per) [0.35]</td>
</tr>
<tr>
<td></td>
<td>π(CO) + πd → π*(PMI-NC) [0.31]</td>
<td>πd → π*(CO)₅ [0.31]</td>
</tr>
<tr>
<td></td>
<td>264 (0.12)</td>
<td>πd → π*(CO)₅ [0.24]</td>
</tr>
<tr>
<td></td>
<td>π(PMI) → π*(PMI) [0.38]</td>
<td>262 (0.22)</td>
</tr>
<tr>
<td></td>
<td>π(CO) + πd → π*(CO)₅ [0.35]</td>
<td>π(Per)_H → π*(Per) [0.37]</td>
</tr>
<tr>
<td></td>
<td>π(PMI) → π*(PMI) [0.24]</td>
<td>πd → π*(CO)₅ [0.28]</td>
</tr>
<tr>
<td></td>
<td>πd → π*(NC) [0.23]</td>
<td>πd → π*(NC) [0.23]</td>
</tr>
</tbody>
</table>

Annotation for the involved orbitals:
- π(PMI) and π(Per) indicate generic occupied orbitals as well as π*(PMI), and π*(Per) are empty ones. Since all of these orbitals are of type π, only H and L are emphasized. Orbital contribution on the nitrile group included when remarkable.
- π(Ph) and π*(Ph) are occupied and empty orbitals centered in the phenylic diimido substituent.
- Other fragments such as C₆F₅ or CO are also used to designate centered π orbitals.
- Other d-orbitals are generally written as πd.
(c) Gold complexes

<table>
<thead>
<tr>
<th>$\lambda$ (f)</th>
<th>$[(\text{PMI-NC})\text{Au(C}_6\text{F}_5)]$</th>
<th>$[(\text{PerNC})\text{Au(C}_6\text{F}_5)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>519 (0.79)</td>
<td>474 (0.69)</td>
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<tr>
<td></td>
<td>$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})_L$ [0.68]</td>
<td>$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})_L$ [0.70]</td>
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<tr>
<td></td>
<td>481 (0.15)</td>
<td>296 (0.25)</td>
</tr>
<tr>
<td>Gas phase</td>
<td>$\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.64]</td>
<td>$\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{Per-NC})$ [0.53]</td>
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<tr>
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<td>325 (0.12)</td>
<td>262 (0.19)</td>
</tr>
<tr>
<td></td>
<td>269 (0.10)</td>
<td>$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})$ [0.49]</td>
</tr>
<tr>
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<td>264 (0.12)</td>
<td>$\pi(\text{Per}) \rightarrow \pi^*(\text{Per-NC})_L$ [0.26]</td>
</tr>
<tr>
<td></td>
<td>$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI})$ [0.48]</td>
<td></td>
</tr>
<tr>
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<td>$\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI-NC})$ [0.30]</td>
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<tr>
<td>CHCl$_3$</td>
<td>527 (1.08)</td>
<td>493 (0.79)</td>
</tr>
<tr>
<td></td>
<td>$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})_L$ [0.71]</td>
<td>$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})_L$ [0.70]</td>
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<tr>
<td></td>
<td>332 (0.08)</td>
<td>297 (0.14)</td>
</tr>
<tr>
<td></td>
<td>$\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.46]</td>
<td>$\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{Per-NC})$ [0.49]</td>
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<tr>
<td></td>
<td>292 (0.16)</td>
<td>266 (0.30)</td>
</tr>
<tr>
<td></td>
<td>$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI})$ [0.40]</td>
<td>$\pi(\text{Per}) \rightarrow \pi^*(\text{Per-NC})_L$ [0.44]</td>
</tr>
<tr>
<td></td>
<td>$\pi(\text{C}_6\text{F}_5) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.37]</td>
<td>$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})$ [0.39]</td>
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<td>262 (0.23)</td>
</tr>
<tr>
<td></td>
<td>288 (0.10)</td>
<td>$\pi(\text{Per}) \rightarrow \pi^*(\text{Per-NC})_L$ [0.52]</td>
</tr>
<tr>
<td></td>
<td>$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI})$ [0.27]</td>
<td>$\pi(\text{Per})_H \rightarrow \pi^*(\text{Per-NC})$ [0.33]</td>
</tr>
<tr>
<td></td>
<td>264 (0.15)</td>
<td></td>
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<tr>
<td></td>
<td>$\pi(\text{PMI})_H \rightarrow \pi^*(\text{PMI-NC})$ [0.53]</td>
<td></td>
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<tr>
<td></td>
<td>$\pi(\text{PMI}) \rightarrow \pi^*(\text{PMI-NC})_L$ [0.34]</td>
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Table S2. Calculated absorption peaks for \([\text{M(CO)}_5(\text{CNR})]\) (M = Cr, Mo, W; R = PMI, Per).

<table>
<thead>
<tr>
<th>R-X</th>
<th>Cr(CO)(_5)</th>
<th>Mo(CO)(_5)</th>
<th>W(CO)(_5)</th>
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<td></td>
<td>Gas phase CHCl(_3)</td>
<td>Gas phase CHCl(_3)</td>
<td>Gas phase CHCl(_3)</td>
</tr>
<tr>
<td>PMI-NC-X</td>
<td>(\lambda) (f)</td>
<td>(\lambda) (f)</td>
<td>(\lambda) (f)</td>
</tr>
<tr>
<td>518 (0.97)</td>
<td>536 (1.14)</td>
<td>526 (0.99)</td>
<td>542 (1.19)</td>
</tr>
<tr>
<td>281 (0.08)</td>
<td>299 (0.16)</td>
<td>300 (0.16)</td>
<td>303 (0.12)</td>
</tr>
<tr>
<td>266 (0.09)</td>
<td>266 (0.07)</td>
<td>267 (0.11)</td>
<td>265 (0.07)</td>
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<tr>
<td></td>
<td>264 (0.12)</td>
<td>266 (0.13)</td>
<td></td>
</tr>
<tr>
<td>Per-NC-X</td>
<td>(\lambda) (f)</td>
<td>(\lambda) (f)</td>
<td>(\lambda) (f)</td>
</tr>
<tr>
<td>468 (0.70)</td>
<td>482 (0.84)</td>
<td>474 (0.75)</td>
<td>487 (0.90)</td>
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<tr>
<td>259 (0.15)</td>
<td>285 (0.11)</td>
<td>286 (0.10)</td>
<td>286 (0.10)</td>
</tr>
<tr>
<td></td>
<td>262 (0.22)</td>
<td>264 (0.37)</td>
<td>262 (0.22)</td>
</tr>
<tr>
<td></td>
<td>256 (0.08)</td>
<td>259 (0.05)</td>
<td>259 (0.07)</td>
</tr>
</tbody>
</table>

Fig. S5 \(^1\)H and \(^{19}\)F NMR spectra

4a
Fig. S6. IR spectra
Fig. S7. Fluorescence decays in dichloromethane, at room temperature.

Mono-exponential and bi-exponential fluorescence decay models were fitted to each decay. Eqn (1) describes the mono-exponential decay model:

\[ I(t) = I_0 \cdot \exp(-t/\tau) \]  

(1)

where \( I_0 \) is the relative intensity, \( t \) is the time and \( \tau \) is the fluorescence lifetime, both expressed in ns. The bi-exponential decay model is expressed by Equation (2) as:

\[ I(t) = A + B_1 \cdot \exp(-t/\tau_1) + B_2 \cdot \exp(-t/\tau_2) \]  

(2)

where \( B_1 \) and \( B_2 \) are the relative intensities associated with two lifetimes, \( \tau_1 \) and \( \tau_2 \), respectively.

Mono-exponential models are normally used to fit fluorescence decay. Bi-exponential fits may be more appropriate for samples containing non-linear decays. Fitting was done using FAST software from Edinburgh Instruments by a least-squares algorithm using a reconvolution approach. In this method, convolution of Equation (1) or (2) with the instrumental response function (IRF) is done prior to evaluating the goodness of fit with a weighted \( \chi^2 \) parameter.

4a
4b

Discrete Components Analysis (Tail fitting)

Fitting range: [150; 2300] channels
$\chi^2$: 1.013

<table>
<thead>
<tr>
<th>Exp Num</th>
<th>B</th>
<th>f</th>
<th>t(ns)</th>
</tr>
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<tbody>
<tr>
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<td>612.6</td>
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<td>4.626</td>
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Background: 0.288
Shift: 0 ns

5a

Discrete Components Analysis (Tail fitting)

Fitting range: [150; 2300] channels
$\chi^2$: 1.027

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Background: 0.138
Shift: 0 ns
**5b**

Discrete Components Analysis (Tail fitting)

Fitting range: [150; 2300] channels

\[ c^2 = 1.039 \]

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<th>t (ns)</th>
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<tr>
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<td>100.0</td>
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Background: 0.791
Shift: 0 ns

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**6b**

Discrete Components Analysis (Tail fitting)

Fitting range: [150; 2300] channels

\[ c^2 = 1.039 \]

<table>
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<th>B</th>
<th>f</th>
<th>t (ns)</th>
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<tbody>
<tr>
<td>1</td>
<td>604.5</td>
<td>100.0</td>
<td>4.149</td>
</tr>
</tbody>
</table>

Background: 0.791
Shift: 0 ns
7b

Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2000] channels

\[ c^2 = 1.032 \]

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<th>t(ns)</th>
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<tbody>
<tr>
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<td>562.8</td>
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<td>3.670</td>
</tr>
</tbody>
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Background : 0.669
Shift : 0 ns

8b

Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2000] channels

\[ c^2 = 1.032 \]

<table>
<thead>
<tr>
<th>Exp Num</th>
<th>B</th>
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<th>t(ns)</th>
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<tbody>
<tr>
<td>1</td>
<td>562.8</td>
<td>100.0</td>
<td>3.670</td>
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</tbody>
</table>

Background : 0.669
Shift : 0 ns
### 9a Discrete Components Analysis (Tail fitting)

- Fitting range: [150; 2200] channels
- $\chi^2$: 1.013

<table>
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<th>t (ns)</th>
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Background: 0.206
Shift: 0 ns

### 9b Exponential Components Analysis (Tail Fitting)

- Fitting range: [100; 1024] channels
- $\chi^2$: 1.201

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<th>fi</th>
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<td>2</td>
<td>1855.0079</td>
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Shift: 0 ns
Decay Background: 5.529
10a

Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2000] channels
\( c^2 \) : 1.062

<table>
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<tr>
<th>Exp Num</th>
<th>B</th>
<th>f</th>
<th>t(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>807.2</td>
<td>100</td>
<td>3.568</td>
</tr>
</tbody>
</table>

Background : 0.210
Shift : 0 ns

10b

Exponential Components Analysis (Tail Fitting)

Fitting range : [100; 1024] channels
\( \chi^2 \) : 1216

<table>
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<th>( B_i )</th>
<th>( f_i )</th>
<th>( t_i ) (ns)</th>
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<td>1447.801</td>
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<td>2</td>
<td>286.7444</td>
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Shift : 0 ns
Decay Background : 4.396
11a

Data and Fitted Curve

Solution

Fit range : [150; 2000] channels
$\chi^2$ : 1.028

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<th>f</th>
<th>t(ns)</th>
</tr>
</thead>
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Background : 0.755
Shift : 0 ns

11b

Data and Fitted Curve

Exponential Components Analysis (Tail Fitting)

Fit range : [110; 800] channels

<table>
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<th>f_i</th>
<th>t_i (ns)</th>
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<td>4437.2231</td>
<td>100.000</td>
<td>1.308</td>
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Shift : 0 ns
Decay Background : 6.141
Discrete Components Analysis (Tail fitting)

Fitting range : [150; 2000] channels

\( c^2 \) : 1.062

<table>
<thead>
<tr>
<th>Exp Num</th>
<th>B</th>
<th>f</th>
<th>t (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>807.2</td>
<td>1000</td>
<td>3.568</td>
</tr>
</tbody>
</table>

Background : 0.210
Shift : 0 ns